

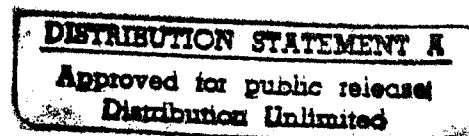
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## IMIDE MODIFIED EPOXY MATRIX RESINS

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D.A. Scola



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16. Abstract This report describes the results of a twelve month program designed to develop tough imide modified epoxy (IME) resins cured by novel bisimide amine (BIA) hardeners. Initial studies of several bisimide amine cured epoxies have been reported by investigators at NASA Lewis. A state-of-the-art epoxy resin, MY720, was used as the epoxy in the former and present study. Three wholly aromatic bisimide amines and one aromatic-aliphatic BIA were evaluated. These were the BIA's derived from the 6F anhydride (3,3'-4,4'-(hexafluoroisopropylidene)bis(phthalic anhydride) and the diamines, 3,3'-diam nodiphenylsulfone (3,3'-DDS), 4,4'-diaminodiphenylsulfone (4,4'-DDS), 1,12-dodecanediamine (1,12-DDA). The BIA's were abbreviated 6F-3,3'-DDS, 6F-4,4'-DDS, 6F-3,3'-DDS-4,4'-DDS, and 6F-3,3'-DDS-1,12-DDA corresponding to the 6F anhydride and the diamines mentioned above. Stoichiometric quantities of the epoxy resin and the BIA's (MY720/6F-3,3'-DDS, MY720/6F-3,3'-DDS-4,4'-DDS, MY720/6F-3,3'-DDS-1,12-DDA and a 50:50 mixture of a BIA and the parent diamine, for example MY720/6F-3,3'-DDS/3,3'-DDS, MY720/6F-3,3'-DDS-4,4'-DDS/3,3'-DDS, MY720/6F-3,3'-DDS-1,12-DDA/3,3'-DDS were studied to determine the effect of structure and composition on resin and composite properties. The effect of the addition (~6%) of two novel commercial epoxies, glyamine 200 and glyamine 100 on the properties of several formulations was also evaluated. The bisimide amine cured epoxies were designated IME's (imide modified epoxy). The physical, thermal and mechanical properties of these novel resins were determined. The levels of moisture absorption in boiling water exhibited by several of the novel IME's were considerably lower than the state-of-the-art epoxies (from 3.2% for the control and state-of-the-art to 2.0 wt% moisture absorption). The char yields are increased from 20% for the control and state-of-the-art epoxies to 40% for the IME resins. The "relative toughness" characteristics of the IME resins were measured by 10° off-axis tensile tests of Celion 6000/IME composites. The results show that IME's containing 6F-3,3'-DDS or 6F-3,3'-DDS-1,12-DDA improved the "toughness" characteristics of the composites (as measured by tensile strength, intralaminar shear strength and shear strain-to-failure) by about 35% (tensile strength) about 35% (intralaminar shear strength) and about 78% (shear strain-to-failure) relative to the control composite prepared from 3,3'-DDS, from 316 to 433 MPa, 54.0 to 73.8 MPa, and 1.08% to 1.93%.					
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# FOREWORD

This work was carried out under NASA contract NAS3-22521 and covers the period September 12, 1980 to December 31, 1981. Initial work on imide modified epoxy matrix resin was reported in NASA CR-165229, Feb. 1, 1981. Dr. Tito T. Serafini was the NASA Program Manager for this initial work. In the present study, Dr. Peter Delvigs was the NASA Program Manager. Dr. Daniel A. Scola was the program manager and principal investigator for United Technologies Research Center.

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## Imide Modified Epoxy Matrix Resins

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## SUMMARY

The objectives of this program are to synthesize and evaluate imide modified epoxy resins cured with novel bisimide amine hardeners in an effort to develop resins with improved toughness characteristics for use as matrix resins in high performance fiber-reinforced composites. The goal is to achieve resins having a twofold increase of the proportional limit strain compared to state-of-the-art epoxy resins. Three wholly aromatic bisimide amines and one aromatic-aliphatic BIA were evaluated. These were the BIA's derived from the 6F anhydride (3,3'-4,4'-(hexafluoroisopropylidene)bis(phthalic anhydride) and the diamines, 3,3'-diaminodiphenylsulfone (3,3'-DDS), 4,4'-diaminodiphenylsulfone (4,4'-DDS), 1,12-dodecanediamine (1,12-DDA). The BIA's were abbreviated 6F-3,3'-DDS, 6F-4,4'-DDS, 6F-3,3'-DDS-4,4'-DDS, and 6F-3,3'-DDS-1,12-DDA corresponding to the 6F anhydride and the diamines mentioned above. Stoichiometric quantities of the epoxy resin and the BIA's (MY720/6F-3,3'-DDS, MY720/6F-3,3'-DDS-4,4'-DDS, MY720/6F-3,3'-DDS-1,12-DDA and a 50:50 mixture of a BIA and the parent diamine, for example MY720/6F-3,3'-DDS/3,3'-DDS, MY720/6F-3,3'-DDS-4,4'-DDS/3,3'-DDS, MY720/6F-3,3'-DDS-1,12-DDA/3,3'-DDS) were studied to determine the effect of structure and composition on resin and composite properties. The effect of the addition (~6%) of two novel commercial epoxies, glyamine 200 and glyamine 100 on the properties of several formulations was also evaluated. The bisimide amine cured epoxies were designated IME's (imide modified epoxy). The physical, thermal and mechanical properties of these novel resins were determined. The levels of moisture absorption in boiling water exhibited by several of the novel IME's were considerably lower than the control and state-of-the-art epoxies (from 3.2% for the control and state-of-the-art to 2.0 wt% moisture absorption). The char yields are increased from 20% for the control and state-of-the-art epoxies to 40% for the IME resins. The "relative toughness" characteristics of the IME resins were measured by 10° off-axis tensile tests of Celion 6000/IME composites.

Based on these measurements, several IME systems IME-9, -14, -18, -10, -13, and -16 exhibited superior mechanical properties than the control. As an example, Celion 6000/IME-9-2B composite exhibited the following 10° off-axis properties. Tensile strength 433 MPa (62.8 ksi) tensile modulus, 80 GPa (11.6 x 10<sup>6</sup> psi), intralaminar shear strength and strain-to-failure, 73.8 MPa (10.7 ksi) and 1.93%, and calculated shear strain-to-failure in resin, 10.6%. For the control composite, these values are 316 MPa (45.8 ksi), 84.8 GPa (12.3 x 10<sup>6</sup> psi), 54.0 MPa (7.84 ksi), 1.08% and 4.65%.

Alteration of the molecular structure of the curing agents appears to be a viable approach toward improving the "toughness", moisture resistance and char yield properties of an epoxy resin system.

## I. INTRODUCTION

This document constitutes the second phase of the final report on a twelve (12) month program to develop tough imide-modified epoxy (IME) resins cured by novel bisimide amine hardeners, initially developed by investigators at NASA Lewis (Refs. 1,2). The first phase of a ten (10) month program has already been reported (Refs. 3,4). State-of-the-art epoxy resins are finding wide applications as matrices in advanced fiber reinforced resin composites which are being used in aerospace vehicles as primary and secondary structural components. However, the brittle nature and poor char forming characteristics of state-of-the-art epoxy resins dictate that changes in molecular structure are necessary to improve toughness and increase char forming ability. Toughness is required for resin matrices used in aerospace structures where high strain-to-failure, durability, and reliability are of prime importance. Higher char yield epoxy resins are desirable because they would provide composites which exhibit improved retention of structural integrity in the event the composite is subjected to a fire.

### 1.1 Objective of the Program

The objectives of this program are to synthesize and evaluate imide modified epoxy resins cured with novel bisimide amine hardeners in an effort to develop resins with improved toughness characteristics for use as matrix resins in high performance fiber-reinforced composites. The goal is to achieve resins having a twofold increase of the proportional limit strain compared to state-of-the-art epoxy resins.

### 1.2 Program Tasks

The work performed under this contract was accomplished in three (3) technical tasks as follows:

Task I - A novel method to synthesize 4,4'-(hexafluoroisopropylidene)bis(0-phthalic anhydride), designated 6F anhydride, was developed. In this task, a novel intermediate, 2-(3,4-dimethylphenyl)-1,3-hexafluoro-2-propanol, designated 6F alcohol, was discovered.

Task II - In this task the novel bisimide amines were synthesized from the 6F anhydride and selected diamines and characterized in sufficient quantities to carry out Tasks III and IV.

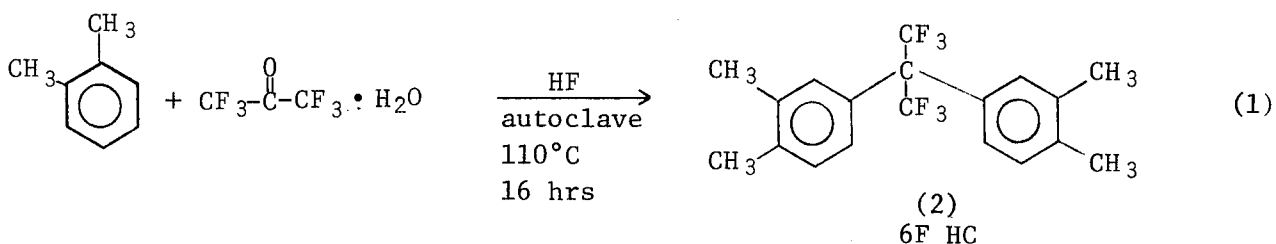


Task III - The bisimide amine cured epoxy resins were synthesized and characterized. Following the characterization of the bisimide amine cured epoxies, 10° off-axis Celion 6000/IME epoxy resin composites were fabricated and tested as a screening method to rate the toughest resins in terms of the 10° off-axis tensile strength, intralaminar shear strength and shear strain to failure.

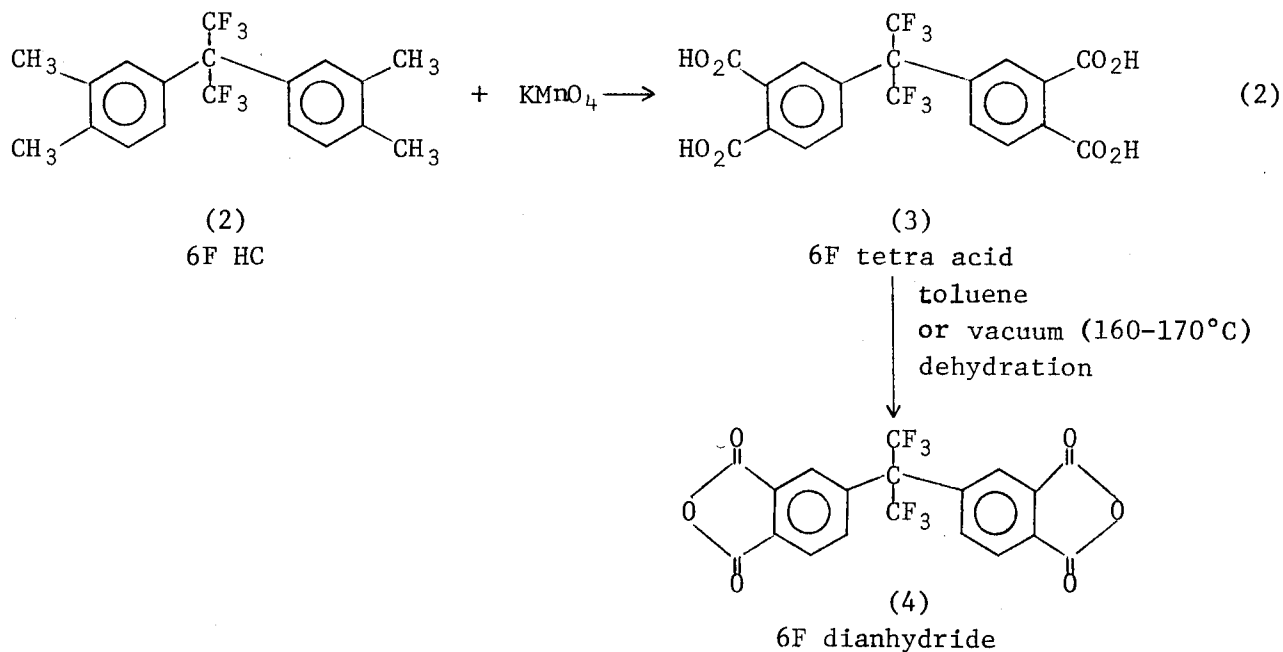
## 2. RESULTS AND DISCUSSION

### 2.1 Synthesis of 4,4'-(hexafluoroisopropylidene)bis(o-phthalic anhydride)

This is an important intermediate for various polymer applications which are not commercially available. The patent literature (Refs. 5,6) reveals that the precursor compound 4,4'-(hexafluoroisopropylidene)bis(o-xylene) (6F HC) is synthesized commercially by reaction of o-xylene with hexafluoroacetone sesquihydrate in an autoclave using hydrogen fluoride as the Friedel-Crafts catalyst.

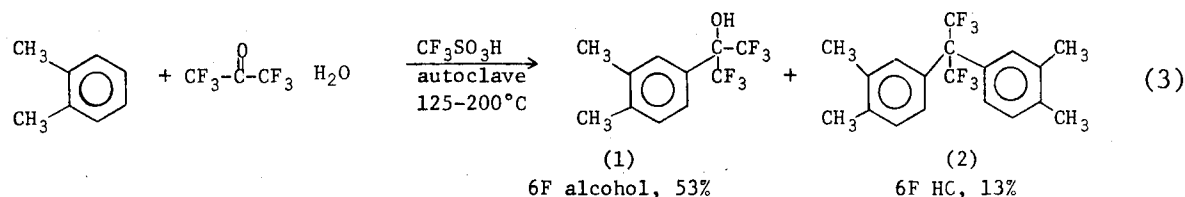


The properties of the product from this reaction were not disclosed but its isolation and oxidation to the 6F tetra acid and subsequent dehydration to the 6F anhydride were described (Refs. 5,6).

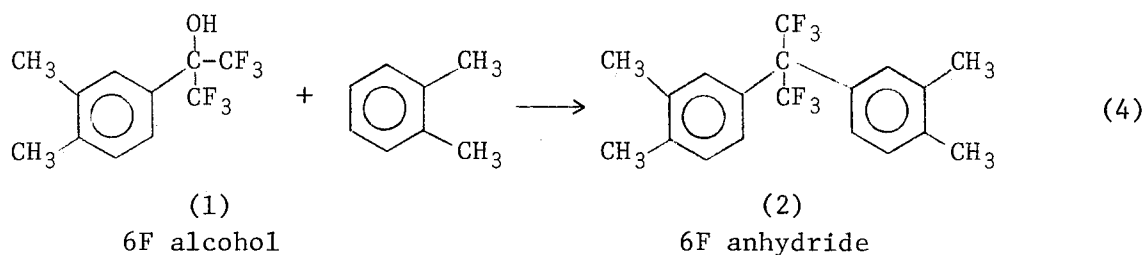


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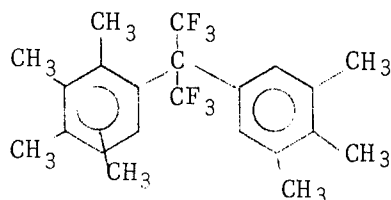
The yield of 6F HC was not defined, nor was the yield of pure 6F anhydride. In the present investigation, a novel method was used to synthesize the 6F HC (2), but the major product was not 6F HC but the 6F alcohol (1) as shown:



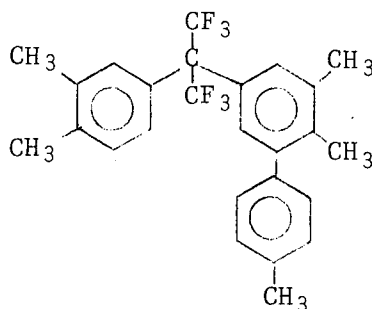
This involved the use of trifluoromethane sulfonic acid as the Friedel-Crafts catalyst. The catalyst has been shown to alkylate aromatics at atmospheric pressure (Ref. 7). However, reaction (3) does not occur at ambient pressure, but only under elevated autoclave reaction pressures. The reaction was carried out at several temperatures, with and without Nafion H, a perfluorinated polymeric sulfonic acid (Table 1). Maximum yield of both products was obtained at the higher temperature (200°C). The 6F alcohol yield was greater than the 6F HC yield by a factor of 4 (53%/13%). The infrared and NMR spectra of the 6F alcohol (1) and 6F HC (2) are shown in Figs. 1 and 2 respectively. The alcohol has not been reported previously. The presence of a strong fluorinated polymeric sulfonic acid (Nafion H) with the  $\text{CF}_3\text{SO}_3\text{H}$  did not appear to affect the yield of either product. An exhaustive study of the reaction parameters was not performed, nor was any attempt made to convert the 6F alcohol to the 6F HC. The formation of 6F anhydride most likely is a two step process involving (1), and o-xylene, reaction (4) but this intermediate has never been isolated by other investigators.



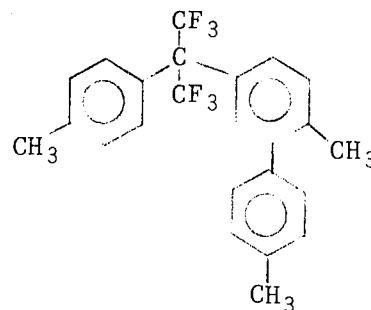
In addition to the novel 6F alcohol and 6F HC compounds, several other fractions were isolated from the chromatographic separation. These fractions were not purified but were analyzed by infrared spectroscopy and elemental analysis. Based on these analyses, molecular structures shown below were assigned to these materials.



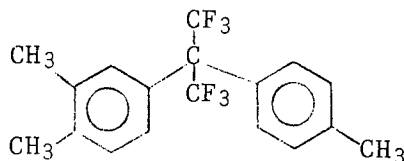
$C_{22}H_{24}F_6$   
yellow oil  
(N203 E-3)



$C_{26}H_{24}F_6$   
brown oil  
N212 D6



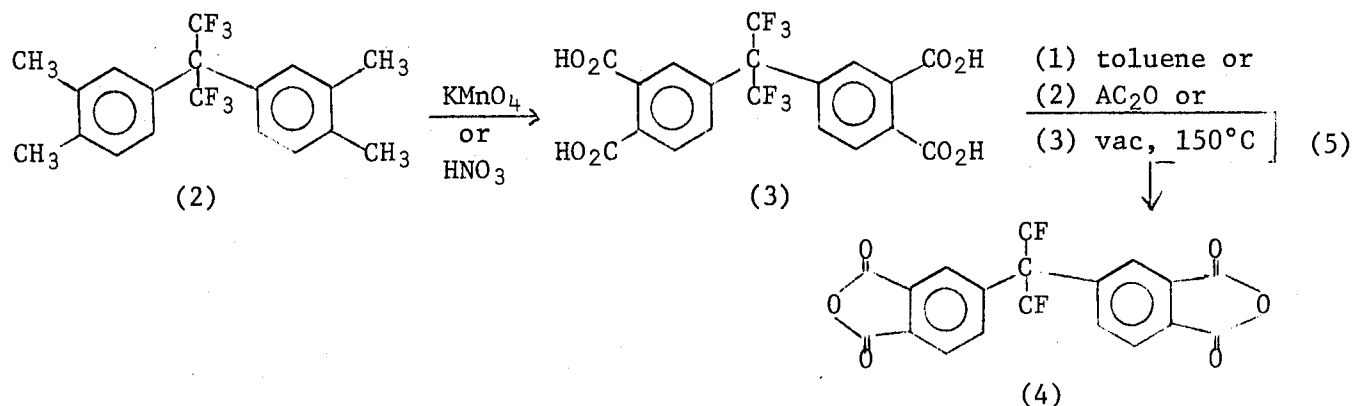
$C_{24}H_{20}F_6$   
brown solid  
N212 D6H



$C_{18}H_{16}F_6$   
brown solid  
N212 D7-10

Each fraction most likely contained mixtures of compounds represented by the structures above and isomers of these structures. However, the 6F alcohol is a novel intermediate which can be a precursor to other polymeric intermediates, such as tricarboxylic acids, amino dicarboxylic acids and other intermediates.

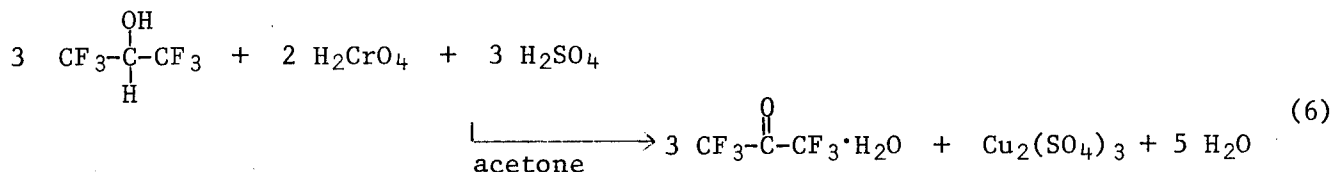
The tetramethyl intermediate was oxidized to the 6F tetra acid using potassium permanganate (Refs. 5,8) (IR, Fig. 4a), or nitric acid (Refs. 6,9) (IR, Fig. 4d). The tetra acid was then dehydrated to the 6F anhydride (4) by three methods:



(1) refluxing in toluene (Ref. 5) (Fig. 5c), (2) acetic anhydride (Fig. 5a), and (3) vacuum heat treatment (Ref. 6) (Fig. 5e).

#### 2.1.1 Attempted Oxidation of Hexafluoroisopropanol to Hexafluoroacetone Sesquihydrate

Hexafluoroacetone sesquihydrate is available commercially but it is extremely expensive. The alcohol is also available commercially at a more reasonable price. The oxidation of the alcohol to the ketone has not been reported. The attempted oxidation of hexafluoroisopropanol to hexafluoroacetone sesquihydrate was carried out at several temperatures by the Jones method (Ref. 10) using chromic acid as the oxidizing agent.



Several runs were made at temperatures ranging from 15° to 100°C, with no success (Table 2). A small quantity of product was obtained in one instance, which exhibited infrared absorption peaks attributed to  $\text{>C=O}$  and C-F groups, but the material was not isolated in pure form.

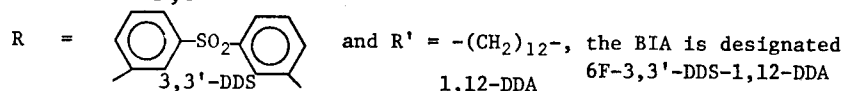
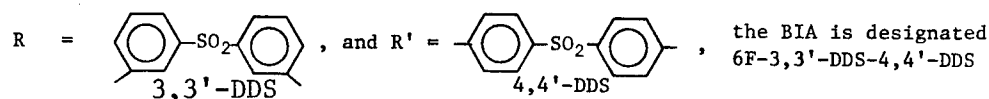
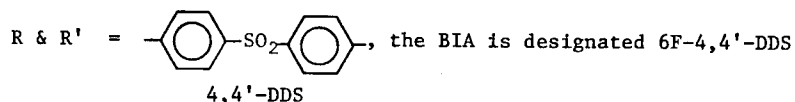
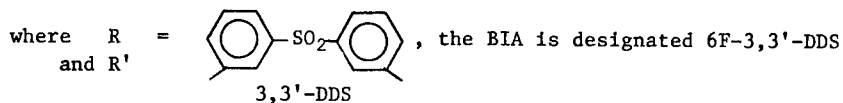
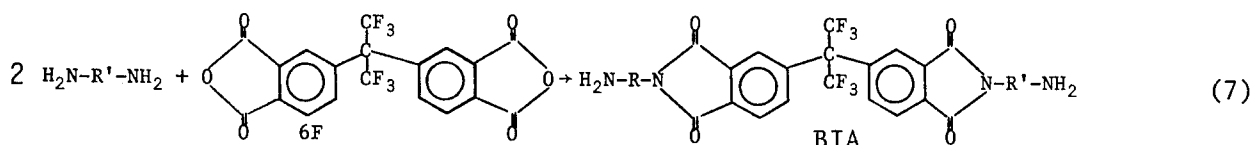
#### 2.1.2 Attempted Synthesis of 4,4'-(hexachloroisopropylidene)bis(o-xylene)

Another approach to obtain the 6F anhydride is from the chlorinated counterpart of the 6F HC (2) by replacement of each chlorine with fluorine. Therefore, a series of Friedel-Crafts (Refs. 11-13) reactions were carried out by reaction of o-xylene with hexachloroacetone under various conditions and with various

catalysts. Table 3 gives a summary of these experiments. In all reactions, dark brown oils or solid and black solids were isolated. Infrared (Figs. 6a,b,c) and NMR analysis indicate that these materials show absorptions characteristic of chlorine containing aromatic compounds and in some cases consistent for the desired product. However, elemental analyses of these products were inconsistent with the desired product. (Table 4).

## 2.2 Synthesis of Bisimide Amines

The structures of the bisimide amines (BIA's), the aromatic and aliphatic diamines from which the BIA's were synthesized and the base epoxy resins used in this program are listed in Table 5. The synthetic route used in preparing the BIA's is represented by this general equation (7).



The general procedure used in the preparation of 6F-3,3'-DDS, 6F-4,4'-DDS and 6F-3,3'-DDS-4,4'-DDS BIA's consisted of refluxing a solution of the aromatic diamine (0.48 mole) and 6F (0.24 mole) in NMP for 2-4 hrs. The reaction mixture was then poured into water while stirring vigorously to yield a crude 6F-diamine product, which was washed several times with hot distilled water to yield product in 90% yield or higher. In the preparation of 6F-3,3'-DDS-1,12-DDA, a solution of the 6F anhydride (0.5 mole) in NMP was added to a stirred

solution of 3,3'-DDS (0.50 mole) and 1,12-diaminododecane (0.50 mole) in NMP (400 ml) over a 1/2 hr period and then the solution was allowed to reflux for time periods up to 24 hrs. The product was isolated in the same manner as for the other BIA's. When the 6F anhydride was used in excess, regardless of the addition sequence, polymeric 6F-3,3'-DDS-1,12-DDA was formed. The infrared spectrum of the bisimide amines are shown in Figs. 7-9. HPLC chromatograms, DSC's, and TGA's of each BIA synthesized in this study are shown in Figs. 10-18.

Elemental analyses and infrared spectra (Figs. 7-9) were consistent for each product. For instance, the completely aromatic bisimide amines 6F 3,3'-DDS, 6F-4,4'-DDS, 6F-3,3'-DDS-4,4'-DDS (Figs. 7a,b,c) showed absorptions at 3500  $\text{cm}^{-1}$ , 3410  $\text{cm}^{-1}$ , 3215  $\text{cm}^{-1}$ , due to primary amine, absorption at  $\sim 1780 \text{ cm}^{-1}$ , 1720  $\text{cm}^{-1}$  due to the imide group, and aromatic substitution patterns at  $\sim 840 \text{ cm}^{-1}$  (due to two adjacent hydrogens) and at  $\sim 870 \text{ cm}^{-1}$  (due to a lone H). Absorption at 1690  $\text{cm}^{-1}$  due to carboxylic acid impurities and at 3700  $\text{cm}^{-1}$  and 3610  $\text{cm}^{-1}$  due to  $\text{H}_2\text{O}$  and/or carboxylic acid impurities were also present. The monomer bisimide amine 6F-3,3'-DDS-1,12-DDA (Fig. 9c) (N 189) shows primary amine absorption at 3500  $\text{cm}^{-1}$  and 3410  $\text{cm}^{-1}$ , in addition to other absorptions expected for this compound. However, the bisimide amines 6F-3,3'-DDS-1,12-DDA represented by N113, 144A, 114, 144B, 140, and 302 (Figs. 2a-d, 3a-b) are polymeric in nature and show very weak absorption at 3500  $\text{cm}^{-1}$  and 3400  $\text{cm}^{-1}$  which may be expected of a polymeric bisimide amine, but also show the absorptions due to the aliphatic groups (3940  $\text{cm}^{-1}$ , 2860  $\text{cm}^{-1}$ ), aromatic groups (850  $\text{cm}^{-1}$ ; 1640  $\text{cm}^{-1}$ , 1610  $\text{cm}^{-1}$ , 1480  $\text{cm}^{-1}$ ) and imide groups (1775  $\text{cm}^{-1}$ ; 1725  $\text{cm}^{-1}$ ).

Furthermore, HPLC analyses (Figs. 10-12) and DSC analyses (Figs. 13-15) revealed that the bisimide amines were not pure compounds, but consisted of bisimide amine and oligomers of bisimide amines. When excess 6F anhydride is added to a refluxing solution of 3,3'-DDS and 1,12-dodecanediamine (1,12-DDA), polymeric bisimide amine and oligomers are the favored products, as expected. When the diamines were added to excess 6F anhydride at refluxing conditions, a similar product mixture was obtained. Treatment of the product mixture with dilute sodium hydroxide to remove unreacted 6F anhydride in both cases do not change the composition. Relatively pure bisimide amines of these reactants were obtained by adding 6F anhydride to a refluxing mixture of 3,3'-DDS and 1,12-DDA in the stoichiometric quantities that favor bisimide amine formation. The HPLC analysis of the three aromatic bisimide amines (Figs. 10a,b,c) show the presence of several components with the major bisimide components eluting between 21 to 67 min depending on the bisimide amine. For the aromatic-aliphatic bisimide amines (N113,N114), the presence of many components and the polymeric nature is indicated by

Figs. 11a and 11b, which represent product before sodium hydroxide treatment and after sodium hydroxide treatment, respectively. The HPLC analysis of a more pure 6F-3,3'-DDS-1,12-DDA bisimide amine (N189) is illustrated in Fig. 12c where the product elutes in 68.48 min. The components eluting between 10 and 14 min correspond to starting materials as determined by standard HPLC's of these compounds.

The DSC analysis further shows the oligomeric and polymeric nature of these bisimide amines. Endothermic and exothermic peaks of each BIA are listed in Table 6. The presence of many endotherms for the aromatic bisimide amines (Figs. 13a,b,c) and the broad nature of the endotherm for the polymeric bisimide amines (Figs. 14a,b,c, 15a,b) is substantiating evidence for this. The sharp endotherm peaks at 220°C (N159), 160°C (N120) and 180°C (N173) are most likely melting points for these bisimide amines.

The DSC of bisimide amine (N189), Fig. 15d, which shows a sharp endotherm at 178°C, and is almost free of other endothermic peaks is also further evidence for its monomeric nature and the purity of this compound. The TGA's (Figs. 16-18) of the aromatic bisimide amines suggest that the thermal stability of these materials is high and might also suggest the presence of oligomers. The TGA's of the aromatic-aliphatic bisimide amines (Figs. 19,20) are lower than the wholly aromatic bisimide amines, as expected.

### 2.3 Composition of Bisimide Amine Cured MY720 Epoxy Resins

Table 5 shows the structures of the uncured epoxy resin and curing agents used in preparing the epoxy resin specimens and graphite fiber reinforced imide modified cured epoxy resin composites. The designation for each material is also listed in Table 5. The composition of each resin system, including the molecular weight of each component, the equivalent ratio of resin to hardener(s) used throughout the study and the epoxy resin system designation are listed in Table 7. The weights of epoxy to hardener(s) used to fabricate small resin specimens and from which portions were taken for cure and characterization studies are also listed in Table 7.

### 2.4 Determination of Resin Thermal Behavior and Cure Cycle

The gel times and time/temperature cure relationship for each resin system (listed in Table 7) were determined. Homogeneous mixtures of the resin systems were required to determine the cure cycle. Two approaches were tested to obtain a homogeneous mixture of the curing agent and MY720 epoxy resin. One involved the use of tetrahydrofuran as solvent to dissolve the mixture followed by removal of the solvent to give a solventless homogeneous powder mixture. The other approach involved heating the mixture at 125°C for 15 min or longer to give a liquefied or homogeneous mixture. The solvent approach worked well for all of the resin systems.



The second method, however, was only applicable to the MY720/DDS resin system. In using the second method for preparing two of the IME resins (IME-9 and -10) the warm mixture was cooled to room temperature, and ball milled in an attempt to produce a homogeneous powder. Material caked along the wall of the ball mill suggesting a heterogeneous mixture had formed. The solventless approach has merit because it would cause fewer problems in fabricating neat resin specimens. However, because of the heterogeneity of the mixture formed, this method was not pursued further for the IME resins. Therefore, the solvent method was used to mix the BIA curing agents and epoxy resins in this study.

#### 2.4.1 Infrared (IR) Study of Cure Reaction

The cure reaction of the resin systems whose compositions are given in Table 7 was studied by infrared spectroscopy. Each of the solventless and homogeneous epoxy-amine mixtures was cured in three stages at 150°C, 177°C and 204°C between two sodium chloride salt plates for intervals of 1 hr, or longer, and the IR spectra after each time interval were recorded.

Previous studies (Refs. 3,4) showed that for the aromatic bisimide amines a cure cycle of 150°C/1 hr + 177°C/2 hrs + 204°C/24 hrs was required for complete cure. The same cure cycle was followed for cure of the bisimide amine cured epoxy in the present study. The IR's of the uncured bisimide amine epoxy systems and cured epoxies are shown in Figs. 19-25.

#### 2.4.2 Differential Scanning Calorimetry (DSC) Studies

The DSC thermal behavior of the uncured MY720/amine mixtures are shown in Figs. 26-29 and listed in Table 8. All appear to undergo volatile evolution at the lower temperatures of 80 and 145°C. This is substantiated by capillary melting point observations (Table 10). The higher endotherms may be associated with the melt process, also substantiated by melting point observations. The first exothermic peak is most likely associated with cure and the last one is most likely associated with decomposition.

#### 2.4.3 Resin Gel Characteristics

The gel characteristics of the control resin and the IME resins were determined by observing the changes in physical appearance which occur while heating the powder (except for resin C-2) at two temperatures, 122°C and 150°C for various time periods. The results are summarized in Table 9.

##### 2.4.3.1 122°C Results

Resin C-2 did not gel up to 1 hr at 122°C, indicating that a temperature higher than 122°C is required for curing of this resin system. Resins IME-10, -11, 11-2 and 11-3 gelled within 30 min and all others exhibited no change in 60 min at 122°C.

#### 2.4.3.2 150°C Results

At 150°C, resin C-2 and IME-9, -10, -11, -12, -11-3, 12-3 showed convenient gel times of between 15 to 30 min. The other resins IME-13, -14, -15, and -16 required at least 1 hr for gelation, but this is not obvious from the 150°C exposure. Pressure is required as indicated in column 3 of Table 9.

#### 2.4.3.3 Under Contact Pressure

Resin specimens were placed in a closed mold at contact pressure, the temperature was raised from RT to the temperatures indicated in Table 9, and held at this temperature under contact pressure for the time periods indicated. This yielded an approximate gelation temperature/time cycle at contact pressure for each resin.

#### 2.4.4 Melt Behavior of IME Resins

The capillary tube melt behavior of the resin systems is listed in Table 10. IME-11 and -12 are rubbery at room temperature and could not be melted in a capillary tube. Attempts to prepare resin specimens by heating the powder to the temperatures indicated in Table 10 resulted in sintered, porous solids, instead of the glassy, clear solids observed in the melting point capillary. Apparently, in a mold poor heat transfer through the powder and cure of the outer surface of the powder prevents melting and consolidation. Resin specimens were prepared by fast heat-up under contact pressure, as described in Table 9.

### 2.5 Resin Characterization

#### 2.5.1 Disk and Rectangular Resin Fabrication

For the resin systems under study, only the control resin is capable of being fabricated into neat resin specimens by pouring the liquid resin mix at 150°C into preheated (150°C) molds. All the other resin systems are solid mixtures at room temperature and efforts to form liquids as one raises the temperature, either slowly or rapidly, in vacuum or at ambient pressure to some softening or melt temperature results in a cured sintered-like specimen or a voidy glassy specimen. As a result, ASTM tensile specimens could be fabricated only for resin C-2. Neat resin disks 2.54 cm diameter x 0.48 cm to 0.635 cm thick samples and rectangular specimens (5.7 cm x 5.1 cm x 0.64 cm) were fabricated by compression molding techniques starting with solvent-free resin powder. The conditions for preparing these specimens are listed in Table 11.

## 2.5.2 Physical Properties of Cured IME Resins

### 2.5.2.1 Density, Coefficient of Thermal Expansion and Cure Shrinkage

The density, coefficient of thermal expansion, and shrinkage due to cure of each IME resin are listed in Table 12. The resins exhibit higher densities than typical epoxies due to the 6F-diamine curing agent. The shrinkage and coefficient of thermal expansion values are typical of epoxy resins.

### 2.5.2.2 Resin Moisture Absorption

Small sections (one-quarter section of a 2.54 cm diameter specimen or a 0.64 cm x 0.64 cm x 0.64 cm specimen from the rectangular specimen) of each resin system were subjected to three conditions of moisture: distilled water at RT for 24 hrs, 95% RH, 82°C to saturation (approximately 8 days) and boiling distilled water for 72 hrs. The results of the moisture gained due to these exposures are listed in Table 13. A comparison of the moisture absorbed by the IME resins for all three conditions with the moisture absorbed by a typical epoxy (3501-6) under the same conditions shows that the IME resins absorb considerably less moisture.

## 2.5.3 Resin Thermal Properties of Epoxy Resins

### 2.5.3.1 Differential Scanning Calorimetry (DSC), Thermomechanical Analyses (TMA) and Thermogravimetric Analysis (TGA)

DSC, TMA and TGA thermograms of the IME resin are shown in Figs. 30-38. Data derived from the DSC, TMA and TGA thermograms of the IME resins are listed in Table 14. The DSC endotherm peak at the highest temperature approaches the glass transition temperature of the resin as defined by TMA. The weight percent loss of each resin system at 300°C and 800°C (in nitrogen) based on TGA data is listed in Table 14. The weight loss experienced by the IME resins is considerably less than the IME control resin C-2 and a typical epoxy.

## 2.5.4 Resin Mechanical Properties

### 2.5.4.1 Tensile Properties

Because of the difficulties encountered in fabricating resin specimens from the IME resin systems, miniature resin systems 5.08 cm long x 0.635 thick x 0.95 cm wide with a 0.32 cm reduced section in the 1.27 cm gage section with a radius in the dogbone section of 5.08 cm were fabricated for most specimens which were capable of being compression molded or melt molded. Control resin specimens were fabricated similarly from a cast resin rectangle (1 1/2" x 2" x 3/8"). The results of the tensile properties are listed in Table 15. The difficulties in fabricating resin specimens and 3.81 cm x 5.08 cm x .64 cm miniature tensile specimens is reflected, in part, by the low values for the control resin and some of the IME resins. These may not reflect the true tensile properties of the resins.

#### 2.5.4.2 Compression Strength

For resin samples, samples of resin were cut from the rectangular specimens for compression measurements. These specimens measured 1.90 cm long x 0.635 cm x 0.48 cm to 0.635 cm. The results of the compression strengths are listed in Table 16. The compression strengths of the IME resins compare favorably with a typical epoxy and with the control resin.

### 2.6 Characterization of Celion 6000/IME Epoxy Resin Composites

#### 2.6.1 Fabrication of Prepreg

Prepregs were fabricated by drum winding epoxy sized Celion 6000 graphite fibers and brush application of an acetone solution of the resin to the dried fiber, calculated to yield a composite with a fiber volume of  $60 \pm 2\%$ . The prepreg tapes were air dried on the drum at room temperature, then vacuum dried at 70°C for 2 hrs to remove traces of acetone, except prepregs containing IME-11, -12, 11-3, 12-3 and 18. These were dried at room temperature in vacuum for 2 hrs, instead of 70°C to prevent advancement of the resin. The plies were stacked unidirectionally and in a few cases in a 10° off-axis configuration and processed by compression molding techniques, as described below. The composition of each Celion 6000/IME composite is tabulated in Table 17.

#### 2.6.2 Processing Parameters for Celion 6000 Epoxy Resin Composites

##### 2.6.2.1 Compression Molding Processing Studies

A series of 5 ply 14.0 cm x 25.4 cm x 0.139 cm were fabricated by compression molding techniques for determination of 10° off axis tensile properties of each system. An open ended mold was used to follow the gelation point by probing the laminate as a function of time at specific temperatures. This information is required to produce void free compression molded composites. Of critical importance in the fabrication process is the time/temperature parameter for the application of pressure in the initial stages of gelation. The composites fabricated and the conditions used in the fabrication process are listed in Table 18. These composites were molded to a constant volume for better control of the final composition (fiber 60 vol %, resin 40 vol %). The unidirectional composites were cut 10° to the fiber direction to measure 10° off-axis properties. Some composites (10.1 cm x 15.24 cm x 0.127 cm) were layed up in 10° mode and cut to produce 10° off-axis specimens.

## 2.6.3 Physical Properties of Celion 6000 Epoxy Resin Composites

### 2.6.3.1 Composition, Density and Ply Thickness

The density, calculated resin and fiber volume percents, and composite ply thickness for the compression molded 5 ply composites (15.24 cm x 25.4 cm x 0.139 cm) are listed in Table 19. In this series the fiber and resin weight before processing were determined, and the final composite weight after removal of excess resin flash was determined to calculate a resin and fiber volume, assuming zero void content.

### 2.6.4 Tensile Properties of 10° Off-Axis Celion 6000/IME Epoxy Resin Composites

The 10° off-axis test specimens and tests were made according to the procedure of Chamis and Sinclair (Ref. 14). This test has been recommended by the authors as a convenient test method for the intralaminar shear characterization of unidirectional composites. This test was selected as a method to evaluate the "relative toughness" characteristics of each system by comparing the intralaminar shear properties and strain-to-failure of each composite system with the C-2 control composite and by comparing the calculated shear strain-to-failure of each resin system for each composite with the control resin and other state-of-the-art resin systems.

In a 10° off-axis tensile specimen, the fibers are aligned at an angle 10° to the uniaxial load direction. When the 10° off-axis specimen is subject to a uniaxial load, a biaxial stress state develops (Ref. 14). This biaxial-stress state consists of three stresses, longitudinal  $\sigma_{\ell 11}$ , transverse  $\sigma_{\ell 22}$ , and intralaminar shear  $\sigma_{\ell 12}$  at the 10° plane. When the uniaxial composite is subject to its maximum load, the intralaminar shear stress  $\sigma_{\ell 12}$  is the only one of these three stresses that is near its critical value and fracture therefore occurs at the 10° plane when  $\sigma_{\ell 12}$  reaches this critical value. The symbol  $\sigma$  denotes stress; the subscript  $\ell$  = ply (unidirectional composite) property; the subscripts 1 and 2 refer to an orthogonal right hand coordinate system, with 1 taken along the fiber direction and 2 along the load direction.

The shear stress in a ply with fibers oriented at a 10° angle from the load direction is given by the following equation (Chamis and Sinclair, Ref. 14):

$$\sigma_{\ell 12} = 0.171 \sigma_{cxx}$$

where  $\sigma_{cxx}$  is the uniaxial fracture strength of the 10° off-axis composite in the x-axis (load) direction. For each composite system, the shear strain-to-failure  $\epsilon_{\ell 12}$ , shear modulus  $G_{\ell 12}$ , and uniaxial tensile strength  $\sigma_{cxx}$  and modulus

$G_{cxx}$  were measured. To relate the shear strain-to-failure of the resin  $\epsilon_{r12}$  in the composite to composite shear strain  $\epsilon_{l12}$ , the relationship (Ref. 15) shown below was used

$$\epsilon_{r12} = \frac{G_f}{G_r} \times \epsilon_{l12}$$

where  $\epsilon_{r12}$  is shear-strain-to-failure in resin,  $G_f$  = fiber shear modulus,  $G_r$  = resin shear modulus. The resin shear modulus is calculated as follows:

$$G_r = \frac{E_r}{2(1+\nu)}$$

where  $E_r$  = resin tensile modulus and  $\nu$  = Poisson's ratio.

$E_r \approx 3.45 \text{ GPa } (0.5 \times 10^6 \text{ psi})$  or value determined experimentally

$\nu \approx 0.35$ ,  $G_f \approx 6.89 \text{ GPa } (1 \times 10^6 \text{ psi})$

$$\epsilon_{r12} = \frac{(1 \times 10^6)}{\frac{E_r}{2(1+\nu)}} = \frac{(10^6)2(1.35)}{E_r} \{\epsilon_{l12}\}$$

$$\epsilon_{r12} = 5.40 \{\epsilon_{l12}\}$$

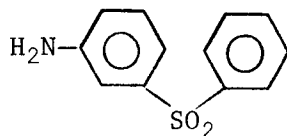
when  $E_r = 3.45 \text{ GPa } (0.5 \times 10^6 \text{ psi})$ .

This enables one to compare resins in composite systems containing the same fiber material and rate the relative performance of a resin in a composite as measured by shear properties.

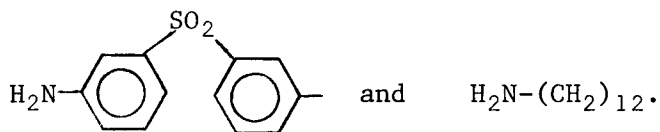
Data for the  $10^\circ$  off-axis tests for samples tested in the "as fabricated" (dry) condition is listed in Table 20. Four  $10^\circ$  off-axis properties, the uni-axial tensile strength, the intralaminar shear strength, composite shear strain-to-failure and the calculated shear-strain-to-failure in the resin of each composite system will be compared with the same properties of the control composite C-2. For the control composite the tensile strength, intralaminar shear strength, shear strain-to-failure in the composite, and shear strain-to-failure in the resin are as follows: 316 MPa (45.8 ksi), 54.0 MPa (7.84 ksi), 1.08% and 4.65%. Comparison of these properties with those properties exhibited by the IME composites, shows that five systems exhibited superior properties in all categories than the control resin. These are listed as follows in order of decreasing

values for each of the above properties: IME-10 2B  $\equiv$  IME 9-2B > IME-14-2 > IME-18-2  $\equiv$  IME-13-2. Two systems, IME-11-D and -16-2 exhibited lower tensile strengths, and intralaminar shear strength than the control composite, but much greater composite shear strain-to-failure and resin shear strain-to-failure than the control composite C-2.

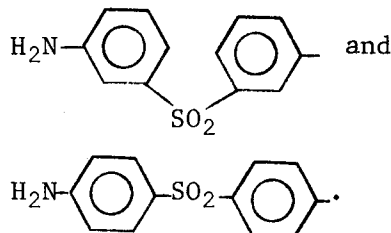
Resins IME-9-2B and -10-2B (in part) were cured by the bisimide amine 6F-3,3'-DDS. These resins contain structural features of the amino diphenylsulfone, shown below.



Resins IME-18-1 and -11-D cured by the bisimide amine (BIA) 6F-3,3'-DDS-1,12-DDA contains structural features of the aminodiphenylsulfone and the aminododecanyl groups.



These combined structural features of these three resin systems appear to contribute to the increase in shear strain-to-failure of the cured epoxy resin relative to the control C-2. The IME-13-2 resin consists of MY720, Glyamine 200 (a prepolymer of bisphenol A and 4,4'-tetraglycidyl (methylenedianiline)) and 6F-3,3'-DDS-4,4'-DDS. The BIA contains structural elements of the isomeric amino-diphenyl sulfone groups

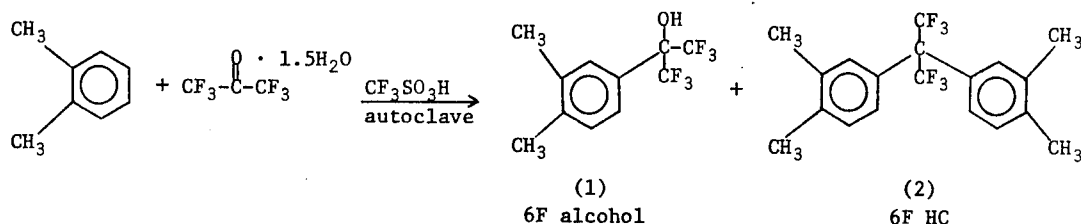


Finally, IME-14-2 and IME-16-2 resin systems contain glyamine 100 (tetraglycidyl of m-xylene diamine), and 6F-3,3'-DDS-4,4'-DDS. The combined molecular components of IME-13-2, -14-2 and -16-2 also appear to contribute to the increased strain-to-failure relative to the control system C-2.

### 3. EXPERIMENTAL

#### 3.1 Synthesis of Intermediates

##### 3.1.1 Synthesis of 4,4'-(hexafluoroisopropylidene)bis(o-xylene) and (2) 2-(3,4-dimethylphenyl)-hexafluoro-2-propanol (1)



The reaction shown above was run in an autoclave using trifluoromethanesulfonic acid at several temperatures and time periods, with and without Nafion H, a fluoropolymeric sulfonic acid catalyst. A description of the general reaction and workup is described as follows. The actual conditions and product yields for each reaction are listed in Table 1.

o-Xylene (81g, 0.764 mole) was added to the pressure vessel, followed by 30 ml of trifluoromethanesulfonic acid. Following this, hexafluoroacetone sesquihydrate (69.4g, 0.359 mole) was added. Bubbling occurred. The pressure vessel was closed immediately to prevent loss of hexafluoroacetone. The reaction mixture was heated at 125°C for 16 hrs (other temperature and time periods are indicated in Table 1). The reaction was cooled to room temperature, vented to the atmosphere, and then opened. It was poured into a beaker, the vessel was washed with 50 ml o-xylene. The two layers were separated. The bottom layer was washed with o-xylene (25 ml) and o-xylene wash was combined with the top o-xylene layer. This o-xylene layer was washed with water (2 x 25 ml), dried over anhydrous magnesium sulfate, filtered, and concentrated to a clear brown oil (45.6g). The infrared spectrum (Fig. 1a) of this crude oil showed absorptions due to alcohol and fluorinated methyl substituted aromatic hydrocarbon.

The bottom layer was dissolved in water and it was extracted with o-xylene. The extract was added to the upper layer. The water layer was then extracted with ether, dried over anhydrous  $\text{MgSO}_4$ , and then concentrated to a black oily layer. Distillation yielded an almost colorless viscous oil (7.2g), B.P. 110-112°C/1.00 mm Hg, which partially crystallized on cooling in ice. The infrared



spectrum (Fig. 1b) of this mixture indicated that it was a mixture of trifluoromethanesulfonic acid and hexafluoroacetone hydrate. A black residue remained (20.4g) which gave a strong acidic reaction to litmus, indicating that it consists mostly of trifluoromethane sulfonic acid. Water (200 ml) was added to this to yield 1.7g of a black material, m.p. 215-238°C. Elemental analysis of this black material gave a substance with the empirical formula  $C_{10.8}H_{9.9}F_{1.0}O_{1.84}$ . The infrared suggests that it is only aliphatic in nature.

The clear brown oil was vacuum distilled to yield a sweet smelling colorless oil, b.p. 94-95°C/16 mm Hg, 40g (38.5%) (labeled NASA 152A). A dark brown distillation residue (1.1g) remained.

The infrared spectrum of this sweet smelling colorless oil (Fig. 1c) showed sharp bands at 3550 and 3610  $cm^{-1}$ , suggesting the presence of a hydroxyl group; 3025  $cm^{-1}$ , 3095  $cm^{-1}$  due to unsaturated C-H stretch; 2880  $cm^{-1}$ , 2940  $cm^{-1}$  2960 and 2995  $cm^{-1}$  due to aliphatic C-H stretch; 1640  $cm^{-1}$ , 1515  $cm^{-1}$  and 1460  $cm^{-1}$  due to C=C vibrations of an aromatic ring; 1275  $cm^{-1}$  and 1200  $cm^{-1}$  due to C-F stretch; 980  $cm^{-1}$  due to hydroxyl stretch; 900  $cm^{-1}$  due to lone H on an aromatic ring; 825 and 850-860  $cm^{-1}$  doublet due to two adjacent H's on an aromatic ring; 700-755  $cm^{-1}$  due to C-F stretch. The infrared spectrum suggests that the material isolated is the intermediate alcohol (1) shown in the reaction sequence. Except for absorptions due to the hydroxyl band, all other absorptions described above could be derived from compound 2, the desired product.

A dark brown residue from the distillation (1.1g) was dissolved in 30 cc heptane, and chromatographed onto silica gel column by eluting with a 50:50 toluene/ n-heptane solution to yield several fractions which varied in color from colorless to yellow to brown. Fractions 1-6 were concentrated to a pale yellow oil (0.8g) which crystallized on standing at room temperature (m.p. 60-61°C). A portion of this solid was recrystallized from water/ethyl alcohol to yield white crystals, m.p. 75-75.5 (NASA 152H). The same procedure was used to isolate the 6F hydrocarbon in subsequent reactions, except that n-hexane or n-heptane was used as the elutant.

The infrared spectrum of compound 2 (Fig.1d) showed aromatic absorption at 3040  $cm^{-1}$ ; strong aliphatic absorptions at 2995, 2960, 2940 and 2880  $cm^{-1}$ ; strong aromatic absorption at 1620  $cm^{-1}$ , 1580  $cm^{-1}$ , 1510  $cm^{-1}$  and 1460  $cm^{-1}$ , CF-stretch in the regions 1100  $cm^{-1}$  to 960  $cm^{-1}$ ; absorption at 900  $cm^{-1}$  due to lone H on an aromatic ring and absorption at 820  $cm^{-1}$  due to two adjacent H's on an aromatic ring. The infrared spectrum suggested that this compound is the fluorinated hydrocarbon shown as compound (2).

The proton and  $^{13}\text{C}$  NMR of compounds 1 and 2 gave the following absorptions:

Proton NMR, Compound 1 ( $\text{CDCl}_3$ ), (Fig. 2a)  $\delta$ : 2.21 ( $\text{CH}_3$ 6H, S), 3.48 ( $-\text{OH}$ , 1H, S); 7.07-7.48 (ArH, 3H, Q);

$^{13}\text{C}$  NMR, Compound 1 ( $\text{CDCl}_3$ ), (Fig. 2b)  $\delta$ : 78.03 (C, C-OH) 123.61 (2C's,  $\text{CF}_3$ ), 124.46 (ArH, C-1), 127.66 (ArH, C-2), 137.66 (ArH, C-3), 139.62 (ArH, C-4), 130.37 (ArH, C-5), 128.07 (ArH, C-6), 19.36, 19.89 (2 C's  $\text{CH}_3$ )

Proton NMR, Compound 2 ( $\text{CDCl}_3$ ), (Fig. 2c)  $\delta$ : 2.19 ( $\text{CH}_3$ , 6H, S), 2.22 ( $\text{CH}_3$ , 6H, S), 7.01 (ArH, 6H, S).

$^{13}\text{C}$  NMR, Compound 2 ( $\text{CDCl}_3$ ), (Fig. 2d)  $\delta$ : 19 (2 C's of  $\text{CH}_3$ ), 78 (1 C of  $\text{C}-\text{CF}_3$ ), 118-128 (2 C's of  $\text{CF}_3$ 's), 124-128 (six aromatic carbons).

Elemental analysis of the two compounds (1) and (2) are listed as follows:

Compound 1, calc'd for 6F alc  $\text{C}_{11}\text{H}_{10}\text{F}_6\text{O}$ :

Calc'd: C, 48.54; H, 3.74; F, 41.88  
Found: C, 48.39; H, 3.76; F, 41.90

Compound 2, calc'd for 6F HC,  $\text{C}_{19}\text{H}_{19}\text{F}_6$ :

Calc'd: C, 63.33; H, 5.04; F, 31.58  
Found: C, 63.44; H, 5.01; F, 31.42

The spectroscopic data and elemental analyses show conclusively that the liquid and solid products are compounds (1) and (2) shown above.

The reaction was repeated to either improve the yields of alcohol and/or fluorinated 6F hydrocarbon. The conditions for these reactions and product yields are listed in Table 1.

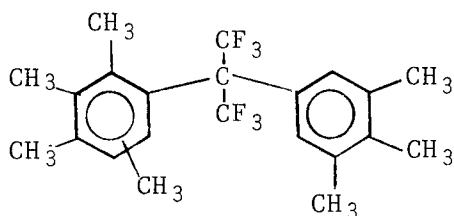
It is clear that the major product is the 6F alcohol. The yield of 6F HC appeared to increase as the reaction temperature increased, but insufficient data prevents a definite conclusion on effects of reaction parameters on 6F HC yield.

From reaction N203 several yellow oil fractions were also isolated from the column chromatographic separation using silica gel. This followed the 6F HC, the main product. The infrared spectrum (Fig. 3a) of these materials looked similar to the IR of the 6F HC except for additional absorptions in the regions 1100 and 1370  $\text{cm}^{-1}$  and in the region between 1006-700  $\text{cm}^{-1}$ . Elemental analyses of oil fraction N203-E-3 and combined oil fraction N203-E-4 thru -9 gave the following results:

N203 E-3, Found: C, 65.30; H, 5.26; F, 28.76

N203 E-4 thru 9, Found: C, 65.80; H, 5.28; F, 28.42.

These analyses fit a compound with the proposed structure:



$\text{C}_{22}\text{H}_{24}\text{F}_6$   
yellow oil

From reaction N209, besides the 6F HC, later fractions from the chromatographic separation produced several yellow oil fractions (N212D1-5) and the last fractions yielded brown oil to brown solid. Fraction N212D6 oil was heated to remove volatiles to yield a glassy solid (N212D6H), m.p. 100-110°C (~0.25g). The infrared spectra (Figs. 3b,c) of fractions N212D6 and N212D6H showed similarities to the yellow oil from the previous reaction (Fig. 3a), except that the brown solid showed very weak absorptions at 1720  $\text{cm}^{-1}$  due to carbonyl group. Other major differences in the spectrum of the brown solid were the very broad absorptions at 1470  $\text{cm}^{-1}$ , 970  $\text{cm}^{-1}$  and 880  $\text{cm}^{-1}$ , and a weak absorption at 820  $\text{cm}^{-1}$ , whereas the spectrum of the yellow 6F hydrocarbon oil (N203E-3, Fig. 3a) showed sharp absorptions in this region.

The purity of the o-xylene used in these reactions was 97%. Therefore, the presence of impurities such as benzene, toluene, tri- and tetramethyl-substituted benzenes, and methylated biphenyls can generate several fluorinated compounds in small quantities, as is indicated by the change in color from colorless to yellow to red to brown in the materials isolated. Impurities in hexafluoroacetone hydrate can also contribute to mixtures produced.

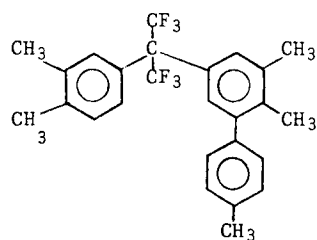
Elemental analysis of the brown oil and brown solid materials gave the following:

N212D6, Found: C, 69.55; H, 5.50; F, 25.12

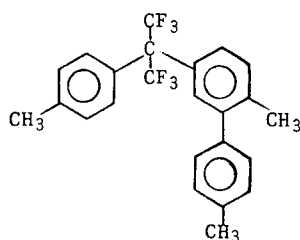
N212D6H, Found: C, 67.58; H, 4.82; F, 26.85.

N212D7-10, Found: C, 60.65; H, 4.67; F, 31.64.

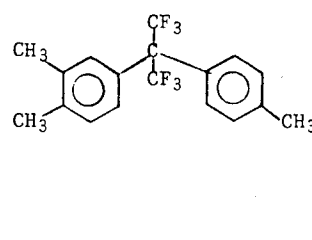
Based on elemental analyses and infrared spectra, structures as shown below are proposed as possible components in the fractions N212D6, N212D6H and N212D7-10:



$C_{26}H_{24}F_6$   
brown oil  
N212D6



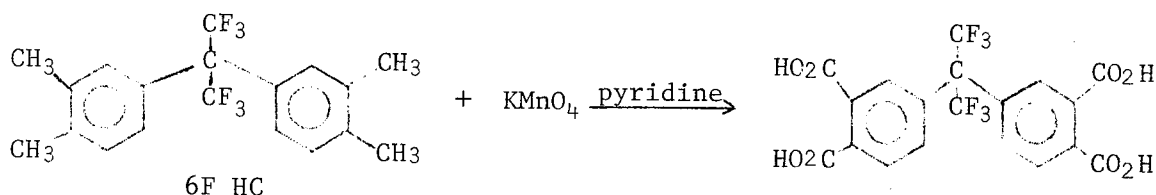
$C_{24}H_{20}F_6$   
brown solid  
N212D6H



$C_{18}H_{16}F_6$   
brown solid  
N212D7-10

### 3.1.2 Synthesis of 4,4'-(hexafluoroisopropylidene)-bis(o-phthalic acid)

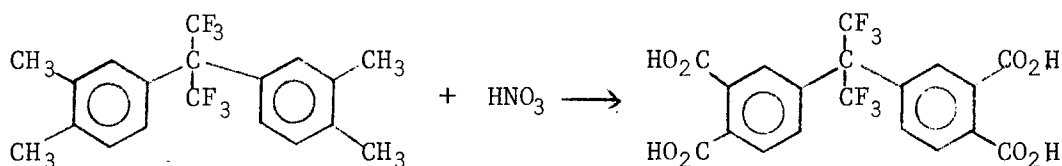
#### KMnO<sub>4</sub> Method



The oxidation procedure of Marvel and Rassweiler (Ref. 8) was followed. A mixture containing 6F HC (1.5g, 0.00416 mole) in 25 ml pyridine and 12.5 ml pyridine was brought to reflux.  $KMnO_4$  (3.10g, 0.0194 mole) was added over a 15 min period. Mixture turned brown after 5 min. Allowed to reflux for another 1.5 hrs. The solution was filtered while hot through a bed of celite filter aid, and the filter bed containing  $MnO_2$  was washed with a hot solution of pyridine/water, 9 ml/3 ml, then with hot water (25 ml). The cloudy filtrate was concentrated to a volume of ~10 ml, and then dissolved in a sodium hydroxide

solution (2.1g in 25 ml). The solution became cloudy as if oil separated. The solution was brought to reflux and  $\text{KMnO}_4$  (4.16g, 0.026 mole) was added within a 20 min period. The solution turned green and then brown. Refluxed 1 1/2 hrs. It was filtered through celite, and washed with a solution of pyridine/water (20 ml/100 ml). The light yellow clear solution was concentrated until no odor of pyridine remained. This required several additions of water, followed by evaporation to a volume ~25 ml. The solution was acidified with conc. HCl to pH = 1. A white oil separated. The solution was concentrated to a solid. The white solid was extracted with boiling acetone to yield 1.8g (90% yield) of straw colored solid, m.p. 210-225°C. A recrystallized sample (ether/hexane) melted at 235-236°C. The infrared spectrum (Fig. 4a) was very similar to the infrared spectrum (Fig. 4b) of an authentic sample. The presence of trace impurities of methylated product due to incomplete oxidation could be detected in the infrared spectrum (Fig. 4c) of the recrystallized sample.

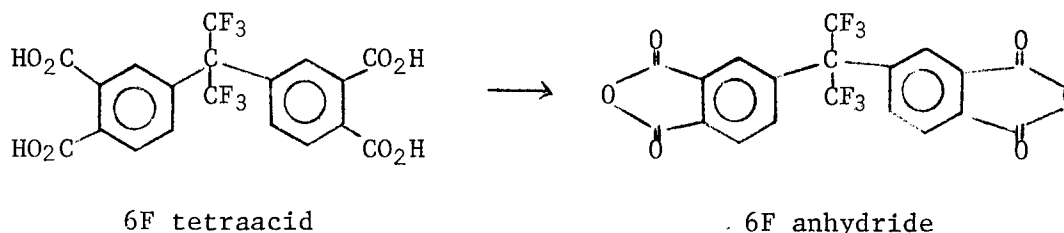
#### Nitric Acid Method



To the 6F HC (1.5g, 0.00146 mole) in an autoclave was added 10.5 ml of 30% nitric acid (0.0583 mole) (Refs. 6,9). The reaction mixture was heated to 200°C for 1 hr. The cooled clear, almost colorless liquid was poured into a beaker and then concentrated on a rotary evaporator to an amber oil, which solidified. The crude solid (2.3g, theory 1.99g) melted at 193-198°C (dec.). The infrared absorption spectrum (Fig. 4d) was similar to infrared spectrum (Fig. 4b) of an authentic sample. No absorptions due to the  $\text{CH}_3$  group could be detected in the infrared spectrum.

The reaction was repeated on a 1.0g scale with 72g of conc. nitric acid at reflux for 3 hrs. The reaction mixture was cooled in the freezer, filtered to remove small quantity (0.40g) of crystals, m.p. 225-235°C (dec.). The filtrate was concentrated to a dark brown residue (0.32g), which melted at 225-245°C. The total yield of crude product (0.72g) was 54%. The infrared spectrum of both solids was almost identical to the infrared spectrum of an authentic sample.

### 3.1.3 Synthesis of 4,4'-(hexafluoroisopropylidene)bis(o-phthalic anhydride) (6F anhydride)



#### Acetic Anhydride Method

A sample of 6F tetra acid (0.20g) was dissolved in 6 ml of acetic anhydride ( $\text{AC}_2\text{O}$ ), and refluxed for 1 hr. The solution was cooled and then concentrated to a dark brown solid (0.15g), m.p. 225-230°C. A small portion was washed in toluene, to a solid m.p. 240-245°C. The infrared spectrum (Fig. 5a) of the crude material was identical to the infrared spectrum (Fig. 5b) of an authentic sample.

#### O-xylene Dehydration Method

A sample of crude tetra acid (0.50g) was treated in boiling o-xylene for 10 hrs using a Dean-Stark trap. The solution was concentrated to an oil (0.253g, 55%) which crystallized, m.p. 225-250°C. The infrared spectrum of this material was identical to the infrared spectrum of an authentic sample. The 6F anhydride was subjected to vacuum sublimation at an initial temperature of 150°C and increasing to 193°C over an 8 hr period. A total of five fractions were collected. The progress of the purification was followed by infrared spectra and melting point determinations.

<u>Fractions</u>	<u>m.p. °C</u>	<u>Infrared Spectrum</u>
N225-A-4	160-230	6F anhydride, some $-\text{CO}_2\text{H}$ and $\text{CH}_3$ impurity
-A-5	190-215	6F anhydride, some $-\text{CO}_2\text{H}$ and $\text{CH}_3$ impurity
-A-6	223-233	6F anhydride, trace $\text{CH}_3$ impurity
-A-7	227-235	6F anhydride, trace $\text{CH}_3$ impurity
-A-8	223-240	6F anhydride, trace $\text{CH}_3$ impurity

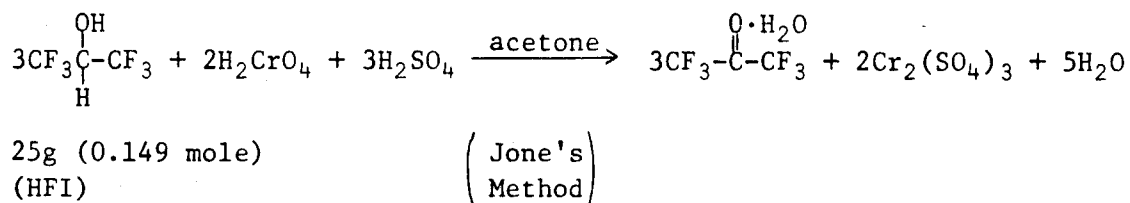
The infrared spectrum (Fig. 5d) of fraction N225-A-8 showed an absorption at  $2960\text{ cm}^{-1}$  due to methyl group impurity, present for unoxidized 6F HC.

### Vacuum Heat Treatment Method

A sample of tetra acid (N225A) film on a sodium chloride salt plate was heated in vacuum as follows: 100°C/15 min + 120°C/15 min + 150°C/30 min. The infrared spectrum after each treatment was obtained to follow the progress of the reaction. The final treatment showed complete conversion of the 6F tetra acid (N225A) to the 6F anhydride (N225AVH), Fig. 5e.

#### 3.1.4 Attempted Oxidation of Hexafluoroisopropanol

Several attempts were made to oxidize 1,1,1,3,3,3-hexafluoro-2-propanol to hexafluoroacetone using chromic acid.

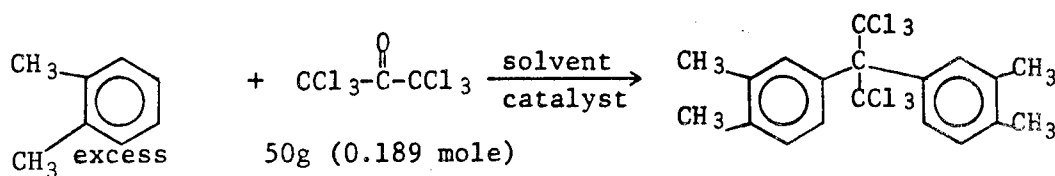


The reaction conditions are listed in Table 2.

The reaction was carried out by dissolving the hexafluoroisopropanol (25g, 0.149 mole) in dry acetone (50 ml) and slowly adding a solution of chromic oxide (9.79g, 0.098 mole) in 70 ml H<sub>2</sub>O/7 ml conc. H<sub>2</sub>SO<sub>4</sub> dropwise to the stirred mixture at a specific temperature. Two layers developed in most cases, and the solution turned brown or brown-green. Excess chromic acid was reduced by the addition of a few drops of 25% NaHSO<sub>4</sub> solution. The two layers were separated. The organic phase was separated and allowed to concentrate to a solid-oil mixture. This was extracted with ether, the ether extract was dried over MgSO<sub>4</sub> (anhydrous) decanted and then concentrated to an oily residue. In all cases only a small quantity of residue remained. In only one case (NASA 86) was a very small amount of material isolated (3.5g) which by IR indicated that it might have been the hexafluoroacetone hydrate. The infrared of this liquid showed absorptions at 1720 cm<sup>-1</sup> and 1185 cm<sup>-1</sup> which could be attributed to C=O and C-F groups respectively.

#### 3.1.5 Attempted Synthesis of 4,4'-(hexachloroisopropylidene)bis(o-xylene)

Several Friedel-Crafts reactions were carried out



in an attempt to synthesize 4,4'-(hexachloroisopropylidene)bis(o-xylene). The reaction variables of solvent, catalyst and temperature listed in Table 3 were investigated.

Using Nafion H superacid in four types of solvents, o-xylene, nitromethane, carbon disulfide and n-hexane at room temperature or reflux temperature using a Dean-Stark trap to collect water as it formed, yielded dark brown oils in yields ranging from 0.2 to 6.2g. Higher yields in solid form were obtained from the reactions using aluminum chloride or trifluoromethane sulfonic acid as catalyst.

The general procedure used in these reactions was to add the catalyst to a solution of hexachloroacetone in o-xylene, in a flask fitted with a stirrer, reflux condenser, and thermometer. The workup for reactions involving Nafion H was to filter to remove Nafion H. The filtrate was distilled to remove o-xylene and hexachloroacetone. The brown or black residues (oil or solid) were analyzed by infrared spectroscopy and elemental analyses. Reactions carried out in  $\text{SbF}_5$  or  $\text{AlCl}_3$  or polyphosphoric acid required the addition of water (~300 ml) to destroy or dilute the catalyst. The organic layer was separated from the aqueous layer. The organic layer was washed with water (3 x 50 ml) and dried over anhydrous magnesium sulfate. The dried organic layer was filtered to remove drying agent, and distilled to remove o-xylene and hexachloroacetone. The brown or black oil or solids were analyzed by infrared spectroscopy and elemental analyses. Examples of infrared spectra for samples N75A, N75B and N90-8, shown in Figs. 6a,b,c, are typical of the spectra derived from these reaction products.

The infrared (IR) spectra of product from each reaction were very similar with small differences caused by varying amounts of unknown materials. All showed absorptions at  $3030\text{ cm}^{-1}$ ,  $2870\text{--}2990\text{ cm}^{-1}$ ,  $1775\text{ cm}^{-1}$ ,  $1745\text{ cm}^{-1}$ ,  $1720\text{--}1680\text{ cm}^{-1}$  (broad),  $1615\text{ cm}^{-1}$ ,  $1510\text{ cm}^{-1}$ ,  $1445\text{ cm}^{-1}$ ,  $1270\text{ cm}^{-1}$ ,  $1170\text{ cm}^{-1}$ ,  $1130\text{ cm}^{-1}$ ,  $1040\text{ cm}^{-1}$ ,  $880\text{ cm}^{-1}$ ,  $820\text{ cm}^{-1}$  and  $775\text{ cm}^{-1}$ . The IR of material from 75C, 87, 90-6, 90-7, 90-8, also showed strong absorption at  $730\text{ cm}^{-1}$  and  $665\text{ cm}^{-1}$ . The IR of material from 90-1, -2, -3 and -4 showed strong absorptions at  $710\text{ cm}^{-1}$  and  $750\text{ cm}^{-1}$ . The IR of material from 75B showed strong absorptions at  $710\text{ cm}^{-1}$ ,  $730\text{ cm}^{-1}$ ,  $620\text{ cm}^{-1}$  and  $630\text{ cm}^{-1}$ . The IR of material from 107-b showed a strong absorption at  $750\text{ cm}^{-1}$ ,  $715\text{ cm}^{-1}$  and  $690\text{ cm}^{-1}$ . Finally, the IR of material from 111A and 148A showed strong absorption at  $640\text{ cm}^{-1}$ .

The NMR spectra of product from reactions 75B, 87, 90-6, -7 and -8 revealed absorptions at 7.1, 7.3, 2.3, 1.8, 1.4 and 1.1 ppm suggesting the presence of aliphatic and aromatic protons. The NMR spectrum of 75C showed absorptions at 7.0, 8.3 and 2.2, 2.4, 2.5, 1.5 and 0.7 ppm.

Elemental analyses of several samples were carried out. The results are listed in Table 4. The elemental analysis for the desired compound is: % C 49.71, % H 3.95, % Cl 46.34. None of the products corresponded or approached this analysis. It is clear that this approach to obtain the desired product is unsuccessful.

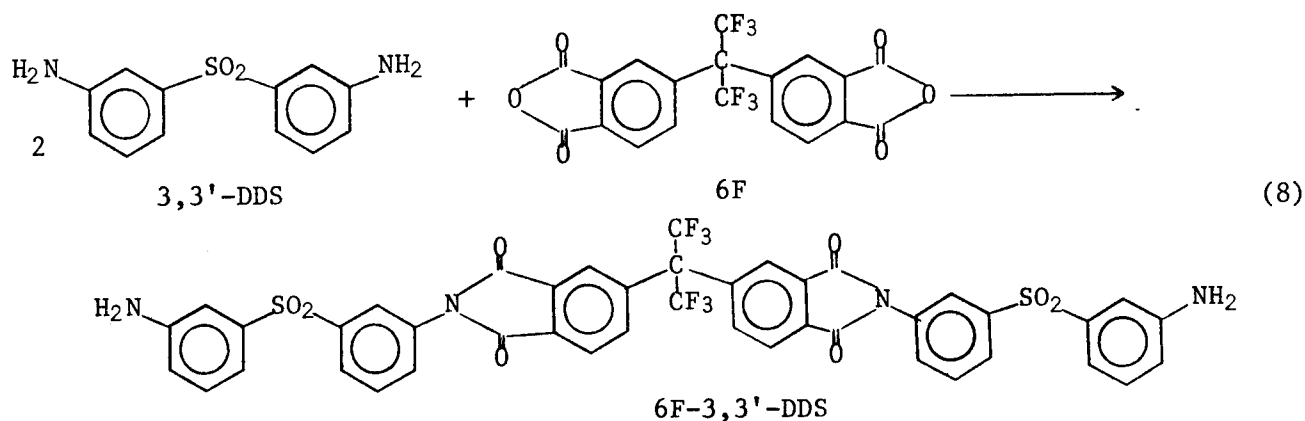


### 3.2 Synthesis of Bisimide Amines (BIA's)

The synthesis, purification, and characterization of the four required bisimide amine (BIA's) hardeners, are described below.

#### 3.2.1 4,4'-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bis[N-3-(m-aminophenyl sulfanilylphenyl)phthalimide], (6F-3,3'-DDS)

The synthetic reaction for this compound is depicted in equation below.



A solution of 113.6g (0.25 mole) of 6F in 250 ml NMP was added dropwise over a one-half hour period to a refluxing solution of 3,3'-DDS (124.2g, 0.5 mole) in 150 ml NMP. The reaction mixture was refluxed for an additional 2 hrs, cooled to room temperature, and poured, while stirring, in water (600g). The off-white solid was filtered and washed several times with distilled water. The solid was placed in 1000 ml water and the mixture was heated to 80°C for 1 hr. The hot slurry was blended in a Waring blender and filtered. Air drying yielded 248.4g of off-white powder. Vacuum drying at 100°C for 2 hrs yielded 211.1g of an off-white powder (93% yield). Reverse phase HPLC analysis of this compound using C<sub>18</sub> Bondapak column (Fig. 10a) showed the presence of several components eluting between 33 to 45 min, but only a trace quantity of 3,3'-DDS eluting in 13.30 min. The DSC (Fig. 13a) showed several endotherms, suggesting the presence of many components.

IR, cm<sup>-1</sup> (dichloromethane solution) (Fig. 7a) 3700, 3610 (S, -OH of CO<sub>2</sub>H), 3080 (W, aromatic -CH), 3500, 3400 (S, amine N-H), 3240 (W, amine N-H), 1790 (m, imide C=O), 1730 (S, imide C=O), 1690 (S, -CO<sub>2</sub>H), 1310 (S, sulfone O=S=O), 1250 (bs, sulfone O=S=O), 1150 (S, sulfone O=S=O), 1110 (m, sulfone O=S=O), 875 (W, 2 adj H's on aromatic ring), 855 (s, 1 lone H on aromatic ring).

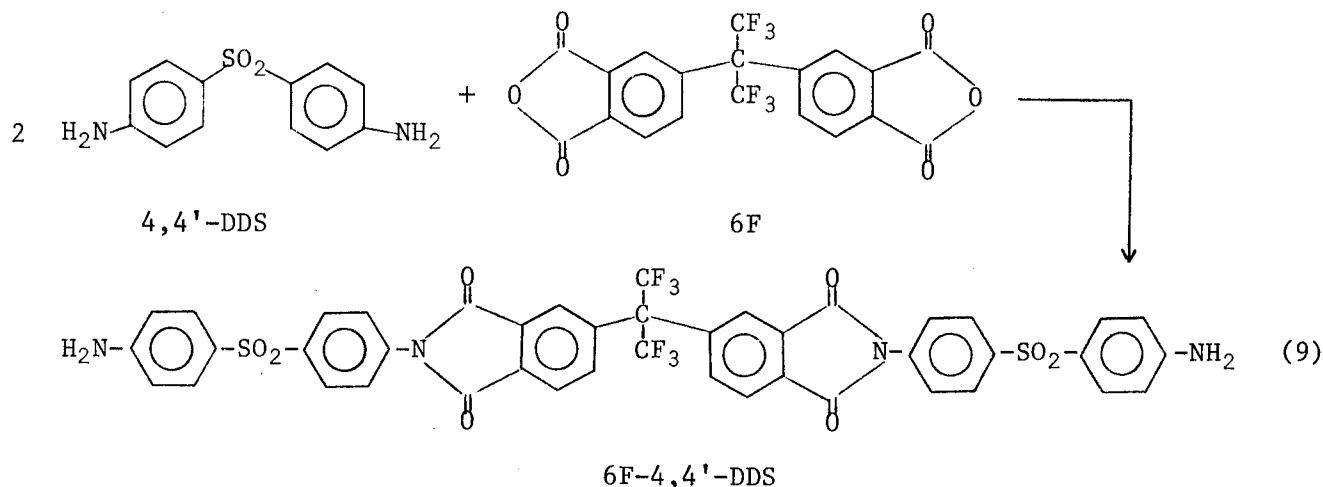
Calc. for  $C_{43}H_{26}N_4F_6S_2O_8$  (MW 904.8)

C, 57.08; H, 2.88; N, 6.20; F, 12.61; S, 7.08

Found: C, 56.95; H, 2.96; N, 6.15; F, 12.54; S, 6.89.

The infrared and elemental analysis are consistent for the bisimide amine, containing carboxylic and other impurities but these techniques cannot differentiate between bisimide amine and oligomers of the bisimide amines. HPLC and DSC reveal that this product contains many minor components with a major component, which is most likely the bisimide amine. This batch was labeled NASA 112. Two additional batches were synthesized, labeled NASA 159A (333g) and NASA 159B (355g) to give a total quantity of 899g.

3.2.2 4,4'-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bis[N-4-(p-aminophenyl sulfonylphenyl)phthalimide], (6F-4,4'-DDS)



To a stirred refluxing solution of 4,4'-diaminodiphenylsulfone (4,4'-DDS, 248.4g, 1.0 mole) in 300 ml of N-methylpyrrolidinone was added a solution of 6F anhydride (227.2g, 0.5 mole) dropwise over a half-hour period. The cooled reaction mixture was added to 1200 ml of distilled water, while stirring vigorously, filtered and air dried. The solid was treated at 80°C in 2000 ml of water for 1 hr. The hot slurry was blended in a Waring blender and filtered and washed with 1000 ml distilled water. The powder was dried at 80°C for 24 hrs followed by vacuum drying at 80°C for 3 hrs to yield 451.4g (99.7% yield), of a pale yellow solid (NASA 120). Reverse phase HPLC analysis of this product using  $C_{18}$  Bondapak column (Fig. 10b) showed the presence of many components, with the major component eluting at between 45 to 67 min. The component eluting at 10.67 min is 4,4'-DDS. This component is present as an impurity in about 10%. The DSC (Fig. 13b) showed several endotherms, suggesting the presence of many components.

IR, ( $\text{cm}^{-1}$ ) (chloroform solution), Fig. 7b, 3700, 3610 (S,  $-\text{OH}$  of  $\text{CO}_2\text{H}$ ), 3060 (W, aromatic C-H), 3450-3360 (W, amine  $\text{NH}_2$ ), 1785 (W, imide  $\text{C}=\text{O}$ ), 1715 (S, imide  $\text{C}=\text{O}$ ), 1690 (S,  $-\text{CO}_2\text{H}$ ), 1310 (S, sulfone  $-\text{SO}_2$ ), 1250 (S, sulfone  $-\text{SO}_2$ ), 1150 (S, sulfone  $-\text{SO}_2$ ), 855 (W, 2 adjacent H's on aromatic ring), 835 (S, 1 long H on aromatic ring).

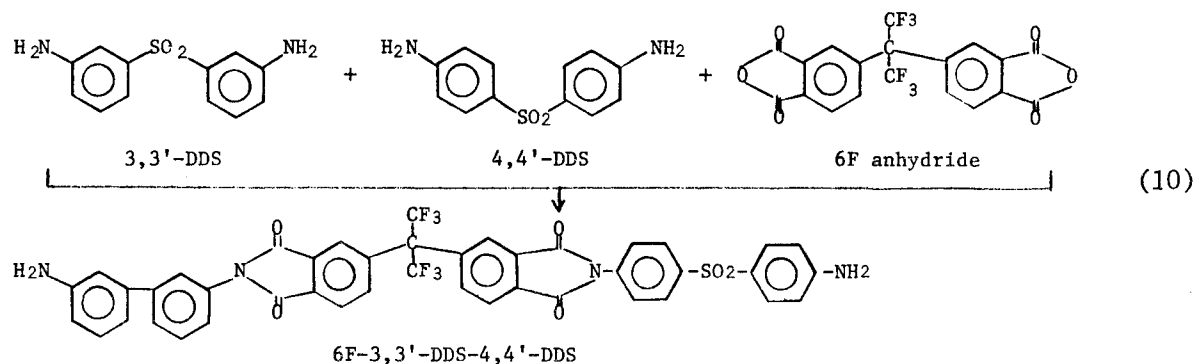
Calc'd for  $\text{C}_{43}\text{H}_{26}\text{N}_4\text{F}_6\text{S}_2\text{O}_8$  (MW 904.8)

Calc'd: C, 57.08; H, 2.88; N, 6.20; F, 12.61; S, 7.08

Found: C, 55.87; H, 3.42; N, 6.14; F, 12.46; S, 5.39

The infrared and elemental analysis (nitrogen and fluorine only) are consistent for the bisimide amine, but these techniques would not differentiate between bisimide amine and oligomers of the bisimide amines. The HPLC and DSC reveal that the product contains many minor components, such as carboxylic acid, with a major component, which is not likely the bisimide amine.

3.2.3 4,4'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-[N-3-(m-aminophenyl)sulfonylphenyl]-N'-4-(p-aminophenyl)sulfonylphenyl bipthalimide] (6F-3,3'-DDS-4,4'-DDS)



The preparation of this compound was carried out on a 0.25 mole scale using equimolar quantities of 3,3'-DDS and 4,4'-DDS (62.1g, 0.25 mole) and 113.6g (0.25 mole) of 6F anhydride, by the procedure for the preparation of 6F-3,3'-DDS described above. The 6F-3,3'-DDS-4,4'-DDS bisimide amine was obtained as a pale yellow solid in almost quantitative yield (210.8g, 93% yield, NASA 173). Reverse phase HPLC analysis of this product using  $\text{C}_{18}$  Bondapak column (Fig. 10c) showed

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#### 6F-3,3'-DDS-1,12-DDA, Method A

A solution of 6F (56.70g, .125 mole) in 150 ml NMP was added dropwise within one-half hour period to a refluxing solution of 3,3'-DDS (15.53g, 0.0625 mole) and 1,12-DDA (11.9g, 0.0625 mole) in 50 ml of NMP. After the addition, the reaction mixture was allowed to reflux for 2 hrs. It was cooled to room temperature, added to ice-water (150g-150g) mixture while stirring. The tan stringy solid which precipitated was filtered and washed with distilled water. The tan solid was treated in boiling water for 1 hr, and the slurry blended in a Waring blender, filtered and air dried. The coarse solid was mixed with water, ground in a ball mill and filtered, and finally washed with water. It was vacuum dried at 100°C for 2 hrs to yield an off-white solid (70.0g) (labeled NASA-113). This is greater than the theoretical yield for the compound, suggesting that polymerization had occurred, and/or that excess 6F is present as an impurity. Reverse phase HPLC analysis of this product using C<sub>18</sub> Bondapak column with a solvent phase undergoing a gradient change 20/80 (THF/H<sub>2</sub>O) → 60/40 (THF/H<sub>2</sub>O) over 45 min revealed that the product contained a large quantity of a volatile component eluting in 1.20 min, and many other components eluting over a time period of 43 min. The volatile component comprised about 46% of the mixture, while another major component comprised 42% of the mixture. The infrared spectrum (Fig. 8a) showed a sharp absorption at 3700 cm<sup>-1</sup> and a broad weak absorption at 3500 cm<sup>-1</sup>, most likely due to carboxylic acid, water and amino groups, 3010, 3060 (W, aromatic C-H), aliphatic absorptions at 2950 and 2910 cm<sup>-1</sup>, imide absorptions at 1765 and 1705 cm<sup>-1</sup> and typical absorption due to aromatic and aliphatic in the higher wavelength regions between 1600 cm<sup>-1</sup> and 600 cm<sup>-1</sup>. DSC (Fig. 14a) showed an endotherm peak at 145°C followed by a broad peak ranging from 200-250°C.

#### Elemental analysis:

Calc'd for C<sub>43</sub>H<sub>42</sub>N<sub>4</sub>F<sub>6</sub>O<sub>6</sub>S: (MW 856.8)

Calc'd: C, 60.28; H, 4.94; N, 6.54; F, 13.30; S, 3.37

Found: C, 58.33; H, 3.62; N, 4.45; F, 17.65; S, 2.49

Elemental, HPLC (Fig. 11a) DSC (Fig. 14a) and IR (Fig. 8a) analyses suggest that unreacted components are present, although the IR showed no signs of 6F or amine impurities. The product (NASA N113) was treated with 200 ml of 4% NaOH solution at room temperature for 2 hrs. The mixture was filtered and washed thoroughly with distilled water (~400 ml) until the washings were neutral. The product was dried at 80°C for 8 hrs to yield 26.0g of tan powder (NASA 144A). HPLC analysis (Fig. 14b) of this product showed only one volatile component eluting at 1.45 min, with the major component eluting at 72.56 min. The infrared (Fig. 8c) was identical to that from NASA 113 (Fig. 8a). However, elemental analysis indicated that monomer impurities were removed and a polymeric material remained behind.

Elemental analysis:

Calc'd for  $C_{43}H_{42}N_4F_6O_6S$  (MW 856.8) bisimide amine

C, 60.28; H, 4.94; N, 6.54; F, 13.30; S, 3.73

Calc'd for  $C_{62}H_{44}N_4F SO_{16}$  polymeric

C, 58.56; H, 3.48; N, 4.44; F, 18.03; S, 2.53

Found: C, 57.66; H, 3.76; N, 4.36; F, 17.30; S, 2.58

This product was not evaluated as a curing agent with epoxy.

The reaction was repeated, but the order of reactant additions was changed. A solution of 3,3'-DDS (15.53g, 0.0625 mole) in 50 ml of warm NMP was added to a refluxing solution of 6F (57.79g, .125 mole) in 170 ml NMP within a 20 min period. The reaction mixture was allowed to reflux for an additional 20 min, then a mixture of 1,12-DDA in 100 ml NMP was added portionwise to the refluxing solution within a 5 min period. The solution was allowed to reflux for 2 hrs, cooled to room temperature and poured, while stirring onto an ice-water mixture (150g-150g). The large chunks were broken up, the mixture was filtered and washed with distilled water. The solid was boiled in water (1000 ml), blended in a Waring blender, filtered and air dried. Finally, it was vacuum dried at 100°C for 4 hrs to yield 77.8g of pale-yellow powder (labeled NASA 114). The infrared spectrum (Fig. 8a) of NASA 113 showed greater absorptions at 3450  $cm^{-1}$  and 3500  $cm^{-1}$  than NASA 114 (Fig. 8c), suggesting the presence of more free amino groups. With this exception, the NASA 114 IR was similar to NASA 113. The DSC (Fig. 14c), HLPC (Fig. 11c) and elemental analyses were also very similar to NASA 113. The elemental analysis is shown below:

Calc'd for  $C_{43}H_{42}N_4F_6O_6S$  (MW 856.8)

Calc'd: C, 60.28; H, 4.94; N, 6.54; F, 13.30; S, 3.73

Found: C, 58.40; H, 3.71; N, 4.56; F, 17.61; S, 2.37

Elemental analysis suggests that unreacted 6F is present as an impurity. Treatment of product NASA 114 with dilute sodium hydroxide as described above for NASA 113 yielded a tan product (31.4g, NASA 144B) which exhibited similar IR (Fig. 8d), DSC (Fig. 14d), HPLC (Fig. 11d) and elemental analysis as NASA 144A.

Elemental analysis:

Calc'd for  $C_{43}H_{42}N_4F_6O_6S$  (MW 856.8) bisimide amine

C, 60.28; H, 4.94; N, 6.54; F, 13.30; S, 3.73

Calc'd for  $C_{42}H_{44}N_4F_2SO_{16}$  polymer

C, 58.86; H, 3.48; N, 4.44; F, 18.03; S, 2.53

Found: C, 57.52; H, 3.73; N, 4.33; F, 17.27; S, 2.48

This product was not evaluated as a curing agent for epoxy.

Method B was repeated using a threefold increase in reactants. A tan solid (97.8g, 61% yield) was isolated (NASA 140). Reverse phase HPLC (Fig. 12a) (analysis showed volatile components eluting at 2.33 and 4.49 min with major components eluting in the region 45 to 65 min. The component eluting at 6.55 min is most likely product, while those eluting earlier (27 to 53 min) are most likely oligomers and polymers. IR,  $\text{cm}^{-1}$  (dichloromethane) (Fig. 9a): 3700, 3610 (w -OH of  $\text{CO}_2\text{H}$ ), 3500, 3410 (W, amine NH), 3050 (W, aromatic CH), 2930, 2860 (S, aliphatic  $\text{CH}_2$ ), 1780 (w, imide C=O), 1720 (S, imide C=O), 1690 (w,  $\text{CO}_2\text{H}$ ), 1340, 1310 (vw, sulfone  $\text{O}=\text{S}=\text{O}$ ), 1150, 1110 (S, sulfone  $\text{O}=\text{S}=\text{O}$ ), 850 (S, 2 adjacent H's on aromatic ring).

#### Elemental analysis:

Calc'd for  $\text{C}_{43}\text{H}_{42}\text{N}_4\text{F}_6\text{O}_6\text{S}$  (MW 856.8) bisimide amine

C, 60.28; H, 4.94; N, 6.54; F, 13.30; S, 3.73

Calc'd for  $\text{C}_{62}\text{H}_{49}\text{N}_4\text{F}_{12}\text{SO}_{16}$  polymer

C, 58.86; H, 3.48; N, 4.44; F, 18.03; S, 2.53

Found: C, 52.88; H, 4.05; N, 4.07; F, 15.87; S, 2.05

The product appears to be mostly polymeric with impurities of 6F carboxylic acid and oligomers.

#### Method C

In an attempt to first prepare the intermediate bisamic acids, 6F (56.8g, 0.125 mole) was dissolved in  $\text{CH}_2\text{Cl}_2$ /acetone (225 ml/550 ml) by heating, then 3,3'-DDS (15.5g, 0.0625 mole) was added at room temperature over a half-hour period. This was followed by addition of 1,12-dodecanediamine (11.8g, 0.0625 mole) within a half hour. A gummy material formed which became an oil. The mixture was refluxed for 4 hrs, solvent removed by distillation. The toluene was added and the mixture was refluxed to remove water using a Dean-Stark tube. The IR of the small sample indicated that only bisamic acid was present. Toluene was distilled and replaced with NMP (300 ml) and the mixture was refluxed 2 hrs. The cooled reaction mixture was poured onto ice/water (150g/150g), and filtered. It was purified by boiling in water, filtered and dried at  $100^\circ\text{C}$  overnight. It was purified again by boiling water, cooled; salt (NaCl) was added to break the emulsion, without success. The mixture was acidified, filtered and the tan product dried at  $60^\circ\text{C}$  overnight to yield 16.0g of product (NASA 119B). This material was not used as a curing agent.

#### Method D

The reaction was repeated by adding a solution of 6F (227.16g, 0.5 mole) in 600 ml NMP to a refluxing solution of 3,3'-DDS (31.06g, 0.125 mole) and 1,12-dodecanediamine (23.0g, 0.125 mole) in 200 ml NMP over a half-hour period. The

reaction mixture was refluxed 2 hrs, cooled to room temperature, added to 800 ml of distilled water while stirring to yield a tan solid. This was filtered, washed with distilled water, purified in 2000 ml of hot water (80°C) by treating portions at a time in a Waring blender. The treated product was filtered, dried at 80°C for 3 hrs, then in vacuum at 50°C for 72 hrs to a yield tan solid (204.0g, 95% yield, NASA 302A). Reverse phase HPLC analysis (Fig. 12b) of this product using C<sub>18</sub> Bondapak column revealed the presence of many components, with two major components eluting at 31.44 and 71.98 min dominating the mixture. A volatile component is eluted in 1.40 min. The DSC (Fig. 15b) showed three major endotherms, up to 340°C.

IR, cm<sup>-1</sup> (dichloromethane solution) (Fig. 9b): 3700, 3610 (m, -OH of -CO<sub>2</sub>H), 2480, 3410 (w, amine -N-H), 2940, 2870 (s, aliphatic CH<sub>2</sub>), 1780 (m, imide C=O), 1730 (s, imide C=O), 1690 (m, -CO<sub>2</sub>H), 1340, 1300 (m, sulfone O=S=O), 1150, 1100 (s, sulfone O=S=O), 855 (s, 2 adjacent H's on aromatic ring), 840 (m, 1 lone H on aromatic ring).

#### Elemental Analysis:

Calc'd for C<sub>43</sub>H<sub>42</sub>N<sub>4</sub>F<sub>6</sub>O<sub>6</sub>S (MW 856.8) bisimide amine

C, 60.28; H, 4.94; N, 6.54; F, 13.30; S, 3.73

Calc'd for C<sub>62</sub>H<sub>44</sub>N<sub>4</sub>F<sub>12</sub>SO<sub>16</sub> polymer

C, 58.86; H, 3.48; N, 4.44; F, 18.03; S, 2.53

Found: C, 55.60; H, 3.57; N, 3.76; F, 18.19; S, 1.89

This product appears to contain impurities of carboxylic acid and is polymeric in nature.

#### Method E

The molar quantities were changed to encourage formation of bisimide monomer. To a stirred solution of 3,3'-DDS, 124.2g (0.50 mole) and 100.0g (0.50 mole) of 1,12-diaminododecane in 400 ml of N-methylpyrrolidinone was added a solution of 6F anhydride (227.1g, 0.5 mole) in 600 ml N-methylpyrrolidinone over a one-half hour period. The solution was allowed to reflux for 24 hrs, cooled to room temperature, and then added slowly to 1600 ml of distilled water while stirring vigorously. The tan-viscous semi-solid material was filtered and washed with water. It was blended in ice cold water (2000 ml) using a Waring blender, filtered and washed with water. Then it was treated in water at 80°C (2000 ml), filtered, and washed with water. It was air dried and finally dried in a vacuum oven at 90°C for 10 hrs to yield 361g of off-white solid (84% yield) (NASA 189).



Reverse phase HPLC analysis (Fig. 12c) of this product using C<sub>18</sub> Bondapak column with a solvent phase undergoing a gradient change 20/80 (THF/H<sub>2</sub>O)→60/40 (THF/H<sub>2</sub>O) over 75 min revealed the presence of primarily two components, one eluting in 13.70 min which is 3,3'-DDS and the product component eluting in 68.36 min. DSC (Fig. 15c) showed a minor endotherm at 90°C with a sharp endotherm at 168°C, which is attributed to the melting point.

IR, cm<sup>-1</sup> (chloroform solution, Fig. 9c), 3700, 3660 (W, -OH of -CO<sub>2</sub>H), 3060, 3020 (W, aromatic C-H), 3490, 3415 (W, amine -NH<sub>2</sub>), 2950, 2880 (S, aliphatic -CH<sub>2</sub>), 1785, 1725 (S, imide >C=O), 1695 (W, -CO<sub>2</sub>H), 1350 (S, sulfone O=S=O), 1310 (S, sulfone O=S=O), 1150 (S, sulfone O=S=O), 1115 (S, sulfone O=S=O), 855 (S, 2 adjacent H's on aromatic ring).

Elemental analysis:

Calc'd for C<sub>43</sub>H<sub>42</sub>N<sub>4</sub>F<sub>6</sub>O<sub>6</sub>S (MW 856.8) bisimide amine  
C, 60.28; H, 4.94; N, 6.54; F, 13.30; S, 3.73

Found: C, 60.34; H, 4.90; N, 6.55; F, 13.60; S, 3.51

Product NASA 189 is essentially pure bisimide amine.

### 3.3 Resin Preparation and Sample Fabrication

#### 3.3.1 Preparation of Homogeneous IME-Resin Powders

Approximately 200g portions of powder for each IME resin system listed in Table 7 were prepared by concentration of a solution (50 wt%) of the resin components in tetrahydrofuran. The residual THF solvent was removed in vacuum at 80°C for 2 hrs for all IME resins except IME-11 and IME-12. These were treated at room temperature in vacuum for time required (2 to 24 hrs) to remove traces of solvent. For each IME system, a fine orange-to-red colored powder was obtained, with the exception of IME-11 and -12. For these two systems, a yellow-orange rubbery solid was obtained. These materials were characterized by DSC.

#### 3.3.2 Resin Cure Studies

The melt behavior of each IME resin powder was determined by observation of the behavior of each resin powder system on exposure to an oven previously set at 125 and 150°C. The melt behavior of each was noted (Table 4). Powder samples were placed in a press sandwiched between aluminum foil, and the flow characteristics and time to gelation at 150°C at a pressure of ~6.9 MPa were recorded (Table 9). The melt behavior of each powder system was also determined

by the capillary tube melting point method (Table 10). The thermal behavior of each system was also determined by DSC studies. A DuPont 1090 thermal analyzer attached to a DuPont differential scanning calorimeter was used. A small quantity of powder (5-10 mg) was used for each scan.

### 3.3.3 Fabrication of IME Resin Disks and Rectangular Specimens

Table 7 gives the composition of the resin materials. Several tensile resin specimens of the control resin C-2 (MY720/3,3'-DDS) were fabricated by the casting technique. The aromatic diamine 3,3'-diaminodiphenylsulfone (3,3'-DDS) was dissolved in the epoxy resin, MY720, at 125°C, and poured into preheated (125°C) mold (3.81 cm x 5.08 cm) to yield a thickness of 0.64 cm. The specimens were cured at 150°C/1 hr + 177°C/2 hrs + 204°C/24 hrs and cut into tensile specimens and other samples as required.

The fabrication procedure for each resin system is listed in Table 11.

Resin disks (2.54 cm diameter x 0.60 cm thick) and rectangular specimens (3.8 cm x 5 cm x ~0.64 cm) of several IME resins were fabricated by compression molding techniques by following the gel point as the temperature approached 150°C in the mold. Resin power (5.0g for the 2.54 diameter mold, 20g for the rectangular mold) was placed into the mold. The assembly was placed into a preheated press, a pressure of 6.89 MPa was applied to consolidate the powder. Pressure was released, and the specimen was then compression molded according to the details in Table 11. At gelation, pressure (1.38 MPa) was applied, and the resin was cured at 150°C for 1 hr followed by treatment at 177°C/2 hrs, and finally postcured at 204°C for 24 hrs.

### 3.3.4 Fabrication of Test Specimens

Compression specimens ~0.60 cm x 0.60 cm x 1.90 cm and tensile specimens 0.95 cm x ~0.64 cm x 5.08 cm were cut from the rectangular specimens. The tensile specimens were dogboned to produce a center gage section of about 1.25 cm in length with a thickness of about 0.47 cm and a radius of 5.08 cm. Small specimens 0.64 x 0.64 x 0.64 cm were also fabricated for moisture absorption, DSC, TMA and TGA studies.

## 3.4 Characterization of IME Epoxy Resins

### 3.4.1 Physical Properties

Density was determined by measuring the volume of a symmetrical sample, and then determining the weight of the sample. The density was calculated as follows: density = weight in grams/volume (cc) = g/cc. The cure shrinkage of

each resin system was determined as follows: % shrinkage = diameter of mold (RT) - diameter of resin spec (RT)/diameter of mold (RT). The coefficient of thermal expansions were determined on 0.64 cm x 0.64 cm x 0.64 cm to 1.00 cm length specimens (cut from the 2.54 cm diameter disks or from the rectangular specimen) on the DuPont 1090-DMA thermal analysis unit in the expansion mode.

#### 3.4.2 Thermal Properties

A DuPont 1090 thermoanalyzer equipped with a 943 thermomechanical analyzer (TMA) and a DuPont thermogravimetric analyzer (TGA) were used to determine the glass transition temperature (T<sub>g</sub>) and weight losses in air as a function of temperature of each resin specimen. The DSC behavior was also determined on a DuPont 1090 thermoanalyzer equipped with a DuPont differential scanning calorimeter (DSC).

The anaerobic char yield of each resin sample was determined in nitrogen by the TGA technique up to a temperature of 800°C.

#### 3.4.3 Mechanical Properties

Tensile specimens of the control resin were measured according to ASTM D638-68 at a crosshead speed of 0.127 cm/min. Miniature dogbone tensile specimens of the control and IME resins were cut from 0.95 cm x 5.08 cm x 0.64 cm coupons. Final dimensions of the test specimens were 5.08 cm long x .635 cm thick, having a 0.32 cm reduced section (width) in the 1.27 cm wide gage section with a radius in the dogbone section of 5.08 cm. The samples were tensile tested at a crosshead speed of 0.127 cm/min.

Compression strength tests were made on specimens which measured 0.64 cm x 0.64 cm x 1.90 cm long, and were cut from the 2.54 cm diameter disks or rectangular specimens. Except for the sample size, the samples were tested according to ASTM D695-69 at a crosshead speed of 0.127 cm/min.

### 3.5 Characterization of IME Epoxy Resins in Composites

#### 3.5.1 Celion 6000/IME Tape and Composite Fabrication

For each composite specimen fabricated, a calculated and measured quantity of epoxy resin was used to give a composite with 60 vol % fiber and 40 vol % resin. This was accomplished by applying, by brush, a solution of the resin in methylethylketone to a prewound 15.24 cm x 43.2 cm (5.5" wide x 17.0" diameter) Celion 6000 dry tape. A 10% excess of resin was applied to account for loss in transfer and resin bleed-out during laminate fabrication. After application of

the resin solution to the dry tape, the tape was allowed to stand at room temperature for 2 hrs. For each tape, trace solvent was removed in vacuum at 60°C for 2 hrs. The tape was cut into five 25.4 cm (10") plies and stacked in a mold for the compression molding process. Thermocouples for temperature measurements was placed inside the center portion of the bottom and top portions of the mold. The system was then placed in a preheated press, and processed as indicated in Table 18.

### 3.5.2 Composite Characterization Techniques

#### 3.5.2.1 Physical Properties

The density of each composite was determined by the liquid displacement technique. Fiber and resin content was determined by calculation from a known weight of fiber and assuming zero void content.

#### 3.5.2.2 Mechanical Properties

10° Off-Axis Tensile Test - This test was carried out according to the procedure of Chamis and Sinclair (Ref. 14). A rectangular rosette (0°, 45°, 90°) of strain gages (type EA-06-062RB-120) was used. The load versus strain for each strain gage was recorded. The samples were loaded at a rate of 0.254 cm/min (0.1"/min).

#### 4. SUMMARY OF RESULTS

1. A series of bisimide amines (BIA's) were prepared by reaction of 4,4'-(hexafluoroisopropylidene)-bis(o-phthalic anhydride), (6F-anhydride) with diamines such as 4,4'-diaminodiphenylsulfone (4,4'-DDS), 3,3'-diaminodiphenylsulfone (3,3'-DDS), 1,12-dodecane-diamine (1,12 DDA), mixtures of 4,4'-DDS and 3,3'-DDS, and mixtures of 3,3'-DDS and 1,12-DDA.

2. A series of BIA cured N,N'-tetraglycidylmethylenedianiline (MY720) epoxies (IME's) were fabricated in the neat form and characterized. Celion 6000/bisimide amine cured epoxy (IME) composites were also fabricated and characterized.

3. Several of the IME resins were found to demonstrate increased moisture resistance after 72 hrs water boil compared to the control resin MY720/3,3'-DDS and state-of-the-art resins. The moisture absorption was 2.0% for the best IME resins (IME-9, IME-10, IME-11-3, IME-12-3, IME-12D and IME-13) compared to 3.2% for the control and state-of-the-art resins.

4. The char yields (at 800°C in nitrogen) increased from 20% for the control resin and state-of-the-art resins to ~40% for the better IME resins (IME-9, IME-10, IME-11D, IME-13, IME-14).

5. Tensile properties were obtained from miniature tensile specimens. The low tensile properties obtained for the control and IME resins may reflect the difficulties in fabricating miniature tensile specimens of all resins. However, the relatively high tensile strengths (4600-5400 psi) and strain-to-failures (0.83 to 2.20%) of several IME resins (IME-10, IME-13, IME-12 and IME-12-3) over the control resin C-2 (2710 psi and 0.54% respectively), suggests that these resin systems may be tougher than the control system. The compression strengths of the IME resins compare favorably with the control resin C-2 and typical epoxies. This further suggests that the compression properties more nearly reflect the true properties of the resins than do the tensile properties.

6. A 10° off-axis tensile test was used to rate the "relative toughness" or relative performance of a resin in a composite based on intralaminar shear and tensile properties of the Celion 6000/IME composite systems compared to the control composite Celion 6000/MY720-3,3'-DDS. Based on these measurements, several IME systems (IME-9, -14, -18, -10, -13 and -16) exhibited superior mechanical properties than the control. As an example, Celion 6000/IME-9-2B composite exhibited the following 10° off-axis properties: tensile strength, 433 MPa (62.8 ksi), tensile modulus, 80 GPa ( $11.6 \times 10^6$  psi), intralaminar shear strength and strain-to-failure, 73.8 MPa (10.7 ksi) and 1.93%, and calculated shear strain-to-failure in resin, 10.6%. For the control composite, these values are 316 MPa (45.8 ksi), 84.8 GPa ( $12.3 \times 10^6$  psi), 54.0 MPa (7.84 ksi), 1.08% and 4.65%.

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Table 1

Autoclave Reaction Conditions for the Synthesis of  
4,4'-(hexafluoroisopropylidene)bis(o-xylene)

Reaction No.	Time hrs	Temp °C	Catalysts	Product Yield, %	
				6F Alcohol <sup>1</sup>	6F HC <sup>2</sup>
N146	22	125	CF <sub>3</sub> SO <sub>3</sub> H	23	none
N150	16	125	CF <sub>3</sub> SO <sub>3</sub> H/Nafion H	39	1.0
N157	16	150	CF <sub>3</sub> SO <sub>3</sub> H	49	product lost
N165	40	160	Nafion H	14.	none
N203	11	200	CF <sub>3</sub> SO <sub>3</sub> H/Nafion H	52	13
N209	16	160	CF <sub>3</sub> SO <sub>3</sub> H	53	13
	8	200			

<sup>1</sup>based on the initial moles of hexafluoroacetone used

<sup>2</sup>based on moles hexafluoroacetone remaining from moles used to form  
the 6F alcohol

Table 2

## Reaction Conditions for Hexafluoroisopropanol Oxidation Runs

<u>Reaction No.</u>	<u>Temp, °C</u>	<u>Time, hrs</u>	<u>Observations</u>
NASA-74	15	4	brown solution formed (2 layers) no product isolated
-80	50	2	brown solution (2 layers) no product isolated
-82	60	7.5	green solution (2 layers) no product isolated
-84	60	9	green solution (2 layers) 3.5g product, isolated appears to be hexafluoroacetone hydrate
-86	77 (reflux)	13	brown solution (2 layers) no product isolated
-90 (reverse ) (addition)	100 refluxed Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> solution (14.9g, 0.05 mole in some H <sub>2</sub> O, 20g H <sub>2</sub> SO <sub>4</sub> )	3	brown solution (2 layers) no product isolated



Table 3

Friedel-Crafts Reactions of o-Xylene (29.7g, 0.28 mole)  
and Hexachloroacetone (50g, 0.189 mole)

Reaction No.	Reaction Solvent (ml)	Catalyst (g)	Temp °C/hrs	Yield of Product Residue, g
75B	o-xylene (10)	Nafion H (10)	RT/8	0.2 dk brown oil
75C	o-xylene (10)	Nafion H (10) + SbF <sub>5</sub> (5.0)	RT/1	3.5 dk brown oil
87	nitromethane (25)	AlCl <sub>3</sub> (21.9)	reflux/8	6.2 dk brown solid
90-1	o-xylene (10)	Nafion H (10)	reflux <sup>1</sup> /72	1.4 dk brown oil
90-2	nitromethane (25)	"	"	6.2 dk brown oil
90-3	carbon disulfide(25)	"	"	1.4 dk brown oil
90-4	n-hexane (25)	"	"	0.9 dk brown oil
90-6	nitromethane (25)	AlCl <sub>3</sub> (37.4)	RT <sup>2</sup>	2.3 dk brown solid
90-7	carbon disulfide(25)	"	RT <sup>2</sup>	35.9 black solid
90-8	n-hexane (25)	"	RT <sup>2</sup>	13.1 dk brown solid
107-3	o-xylene (39) <sup>3</sup>	polyphosphoric acid (454)	reflux/6	0.5 brown oil
111A	o-xylene (200) <sup>4</sup>	CF <sub>3</sub> SO <sub>3</sub> H (15)	reflux/52	6.0 black oil
148A	o-xylene (34) <sup>5</sup>	CF <sub>3</sub> SO <sub>3</sub> H/auto- clave (30)	125/16	8.8 black solid

<sup>1</sup> refluxed after standing at RT for 2 weeks, with no noticeable change

<sup>2</sup> allowed to stand at RT for 2 weeks

<sup>3</sup> (0.274 mole, CCl<sub>3</sub>COCCl<sub>3</sub> used)

<sup>4</sup> (0.27 mole, CCl<sub>3</sub>COCCl<sub>3</sub> used)

<sup>5</sup> (0.283 mole, CCl<sub>3</sub>COCCl<sub>3</sub> used)

Table 4

Elemental Analysis of Products from Friedel-Crafts  
Reactions of O-xylene and Hexachloroacetone

Reaction No.	%		
	C	H	Cl
75C	84.02	7.69	5.89
97	65.27	5.64	17.93
90-6	69.57	5.84	19.05
90-7	75.04	5.72	14.63
90-8	77.25	6.56	14.21
148C	69.52	5.51	9.08

The elemental analysis for the desired compound is: % C 49.71, % H 3.95, % Cl 46.34. None of the products corresponded or approached this analysis. It is clear that this approach to obtain the desired product was unsuccessful.

**TABLE 5**  
**STRUCTURES OF HARDENERS AND EPOXY RESINS**

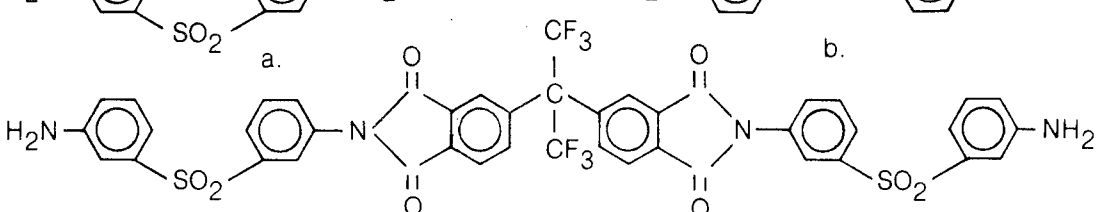
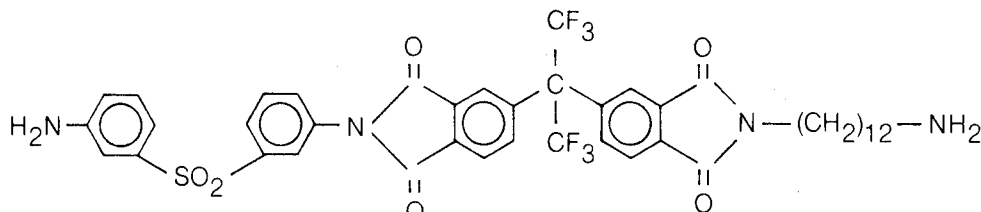
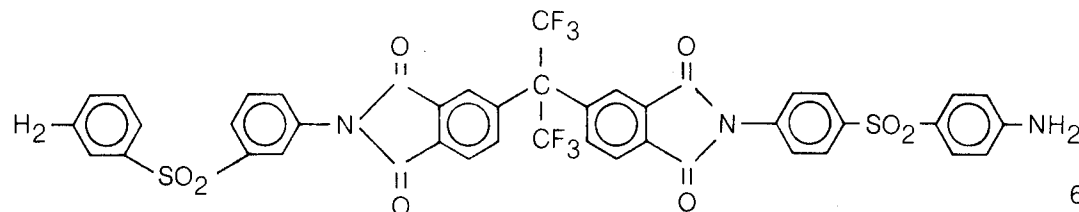
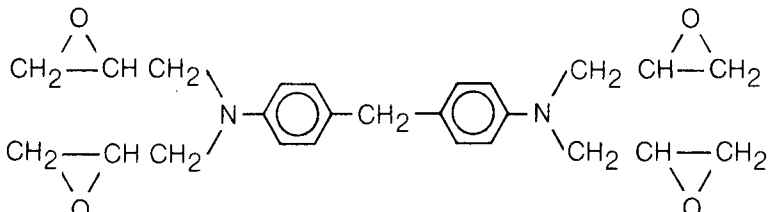
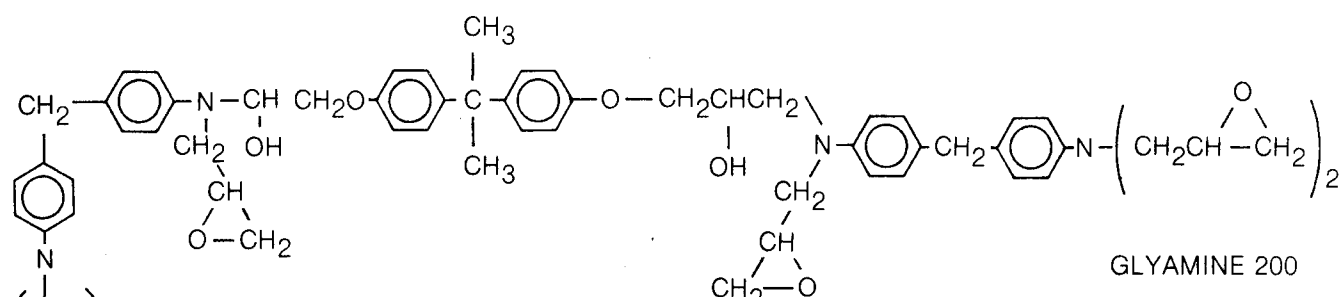
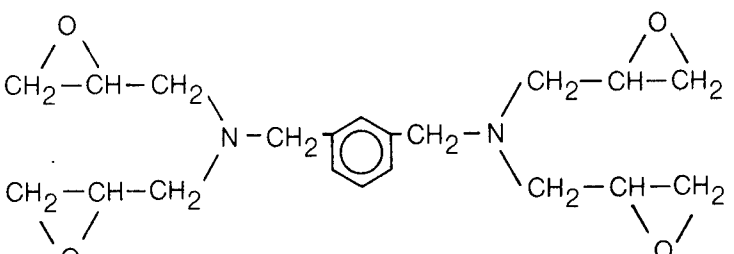
STRUCTURE	DESIGNATION
$\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4-\text{NH}_2$	a. 3,3'-DDS
$\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4-\text{NH}_2$	b. 4,4'-DDS
	6F-3,3'-DDS
	6F-3,3'-DDS-1,12-DDA
	6F-3,3'-DDS-4,4'-DDS
	MY 720
	GLYAMINE 200
	GLYAMINE 100

Table 6

## DSC Behavior of Bisimide Amines

BIA	Endotherms			Exotherms
	°C			
6F-3,3'-DDS (N159)	100 br	160 sh	220 sh	350 br
6F-4,4'-DDS (N120)	150 br	160 sh	240-320 br	360 sh
6F-3,3'-DDS-4,4'-DDS	80 br	180 sh	220 br	360 sh
6F-3,3'-DDS-1,12-DDA (N113)	80 br	160-260 br		290,360 sh
6F-3,3'-DDS-1,12-DDA (114A, NaOH treated)	80 br	160-260 br		290,360 sh
6F-3,3'-DDS-1,12-DDA (N114)	80 br	160-260 br		290,360 sh
6F-3,3'-DDS-1,12-DDA (N144B, NaOH treated)	80 br	160-260 br		290,360 sh
6F-3,3'-DDS-1,12-DDA (N140 NaOH treated)	80 br	160-260 br		290,360 sh
6F-3,3'-DDS-1,12-DDA (N302)	90 sh	168 shr	310 sh	360 sh
6F-3,3'-DDS-1,12-DDA (N189)	90 br (weak)	168 shr		360 sh

br = broad peak

sh = sharp peak

Table 7

## Composition of MY720/IME Resins

Resin No.	Composition	Molecular Weights	Equivalents of each		Ratio of Equivalents	Component Weights (g)
			Component			
Control G-2	MY720/3,3'-DDS	(500/248.4)	0.96/0.96	1:1		120/60
IME-9	MY720/6F-3,3'-DDS (NASA 159A)	(500/904.8)	0.256/0.256	1:1		32/57.9
IME-10	MY720/6F-3,3'-DDS/3,3'- DDS (NASA 159A)	(500/904.8)	0.34/0.152/0.168	2.24:1.00:1.11		42.5/34.3/10.4
IME-11	MY720/6F-3,3'-DDS- 1,12-DDA (Method D, NASA 302)	(500/856.8)	0.52/0.52	1:1		65.0/111.4
IME-11-3	MY720/6F-3,3'-DDS- 1,12-DDA (Method E, NASA 189)	(500/856.0)	0.26/0.196	1.32:1.00		32.5/41.8
IME-11-D	MY720/6F-3,3'-DDS- 1,12-DDA (Method D, NASA 302)	(500/856.8)	0.26/0.208	1.32:1.00		32.5/44.6
IME-12	MY720/6F-3,3'-DDS- 1,12-DDA/3,3'-DDS (Method D, NASA 302)	(500/856.8/248.4)	0.68/0.34/0.34	2:1:1		85.0/72.8/21.1

Table 7 (Cont'd)

Resin No.	Composition	Molecular Weights	No. Equivalents of each		Ratio of Equivalents	Component Weights (g)
			Component			
IME-12-3	MY720/6F-3,3'-DDS- 1,12-DDA/3,3'-DDS (Method E, NASA 189)	(500/856.8/298.4)	0.34/0.128/0.191		2.65:1.00:1.50	42.5/27.3/11.9
IME-12-D	MY720/6F-3,3'-DDS- 1,12-DDA/3,3'-DDS (Method D, NASA 302)	(500/856.8/248.4)	0.34/0.136/0.091		2.5:1.00:1.41	42.5/29.1/11.9
IME-13	MY720/Glyamine 200/ 6F-3,3'-DDS-4,4'-DDS (NASA 173)	(500/1200/904.8)	0.375/0.0595/0.599		6.30:1.0:10.1	46.8/11.9/135.7
IME-14	MY720/Glyamine 100/ 6F-3,3'-DDS-4,4'-DDS (NASA 173)	(500/1200/904.8)	0.375/0.0595/0.599		6.30:1.0:10.0	46.8/5.6/135.7
IME-15	MY720/Glyamine 200/ 6F-4,4'-DDS (NASA 120)	(500/1200/104.8)	0.375/0.0595/0.599		6.30:1.0:10.0	46.8/11.9/135.7
IME-16	MY720/Glyamine 100/ 6F-4,4'-DDS (NASA 120)	(500/408/909.8)	0.375 /0.0595/0.599		6.30:1.0:10.0	46.8/5.6/135.7
IME-18-1	MY720/6F-3,3'-DDS- 1,12-DDA (Method B NASA 144B)	(500/856.8)	0.096/0.104		1.0:1.08	12.0/22.2

Table 8

## DSC Data of Uncured Epoxy Resins

Temp. at Peaks

<u>Resin System</u>	<u>Endotherms, °C</u>	<u>Exotherms, °C</u>
C-2		
IME-9	120,145,170,180	260,>300 <sup>1</sup>
-10	80,140	240,>300 <sup>1</sup>
-11	80,145,160,178	260,>300 <sup>1</sup>
-11-3	60,	280,360
-11-D	160	290,360
-12	65,100	240,360
-12-3	60,120	240,360
-12-D	60,180	260,360
-13	110,130,170,185	260,>300 <sup>1</sup>
-14	60,110,130-190	270,>360 <sup>1</sup>
-15	60,110,130-190	270,>360 <sup>1</sup>
-16	60,90,110,160,180	270,>360 <sup>1</sup>
-18	~160	260,360

<sup>1</sup> stopped DSC at this temperature

Table 9

## Gel Characteristics of IME Resins

Resin System	Gel Time, min		Flow and Gelation Under Pressure (~6.9 MPa) @ 150°C/min
	at 122°C	at 150°C	
Control C-2	no gel, 60	50	flow, gel, glassy, clear/50
IME-9	foam, 1 hr no gelation	30	flow, gel, glassy, clear/30
-10	30	30	flow, gel, glassy, clear/30
-11	60	30	flow, gel, opaque/10
-12	foam, 1 hr no gelation	30	flow, gel, opaque/10
-13	foam, 1 hr no gelation	30, foamed, sintered, no gel apparent	flow, gel, glassy, clear/60
-14	"	"	flow, gel, glassy, clear/60
-15	"	"	flow, gel, glass, clear/60
-16	"	"	flow, gel, glassy, clear/60
-11-3	30	15, opaque	flow, gel, opaque/10
-11-D	60, no change	60, no change	no flow, powder/60
-12-3	30	15, heterogeneous	flow, gel, opaque/15
-12-D	60, no change	60, no change	no flow, powder/60
-18	60, no change	sintered, no gel	flow, gel, glassy, clear/10



Table 10

Capillary Tube Melt Behavior of  
IME Resin Powders

<u>Resin No.</u>	<u>Powder Color</u>	<u>Melt Behavior, °C</u>
IME-9	red-orange	sinters 80, melts 90, foams 110, melt 140
-10	red-orange	sinters 75, melts 90, foams 110, melts 150
-11	yellow	rubbery at RT
-12	yellow	rubbery at RT
-13	red-orange	foams 105, liquefies 170
-14	"	"
-15	"	"
-16	"	"
-11-3	pale yellow	partial melt 75, 2 phases
-11-D	dark red	no melt up to 310
-12-3	pale yellow	partial melt 75, 2 phases
-12-D	dark red	no melt up to 310
-18	red-orange	no melt up to 310

Table 11  
Processing Parameters to Fabricate Epoxy Resin Specimens

<u>Resin No.</u>	<u>Resin Powder Preparation</u>	<u>Cure Cycle</u>
Control C-2	Mix MY720 + 3,3'-DDS, heat to 150°C, pour liquid into preheated (150°C) mold	150°C/1 hr + 177°C/2 hrs, postcure 204°C/24 hrs
IME-9	Dissolved resin components in THF (50 wt%), removed solvent at 70°C, 2 hrs, then at RT, vac. overnight	Compression molded. Placed in pre-heated press at 150°C, consolidated sample at 0.69 MPa and removed pressure, raised T to 150°C, applied 0.69 MPa (no flow), raised T→177°C, hold 177°C 2 hrs, postcured 204°C/24 hrs
IME-10	Same as IME-9	Compression molded. Placed in pre-heated press at 150°C, consolidated sample at 0.69 MPa and removed pressure, raised T→146°C, gelation occurred, applied 0.69 MPa, hold 150°C, 1 hr, raised T→177°C, hold at 177°C 2 hrs, postcured 204°C/24 hrs
IME-11	Dissolved resin components in THF (50 wt%), removed solvent in air at RT then RT, vacuum 24 hrs	Same as IME-10, except at gelation (150°C), applied 3.45 MPa, hold 1 hr, 150→177°C, hold 177°C 1 hr, 3.45 MPa postcure 204°C/24 hrs
IME-11-3	Same as IME-11	Same as IME-11
IME-11D	Same as IME-11	Same as IME-11 except that at 150°C, no flow, applied 0.69 MPa and followed cycle as indicated
IME-12	Same as IME-11	Same as IME-11
IME-12-3	Same as IME-11	Same as IME-11

Table 11 (Cont'd)

<u>Resin No.</u>	<u>Resin Powder Preparation</u>	<u>Cure Cycle</u>
IME-12-D	Same as IME-11	Same as IME-11 except at 150°C no flow, but applied 0.69 MPa and followed cycle as indicated
IME-13	Same as IME-11	Same as IME-11
IME-14	Same as IME-11. In addition treated powder at 150°C, 15 min	Same as IME-11
IME-15	Same as IME-11. In addition, treated powder at 120°C, 15 min	Same as IME-11 except used 3.45 MPa pressure
IME-16	Same as IME-11. In addition, treated powder at 150°C, 15 min	Same as IME-11 except no flow, but applied 3.45 MPa pressure at 150°C, and followed cycle as indicated but at higher pressure

Table 12

Some Physical Properties of Cured  
Neat Resin Systems<sup>1</sup>

Resin No.	Density g/cc	Shrinkage Due to Cure, %	Coefficient of Thermal Expansion cm/cm/°C $\alpha \times 10^5$
C-2(control resin)	1.24	0.80	4.87
IME-9	1.33	0.74	5.25
-10	1.29	0.80	5.80
-11	-	-	6.80
-11-3	-	-	-
-11-D	1.32	-	7.38
-12	-	-	5.79
-12-3	1.27	0.64	-
-12-D	1.28	-	5.89
-13	1.34	0.74	5.88
-14	1.35	-	6.19
-15	1.35	-	7.64
-16	1.35	0.44	-

<sup>1</sup> See table 11 for exact cure cycle. Except for resin C-2, samples were compression molded at 0.69 to 3.45 MPa pressure, depending on resin system. Pressure was applied at about 150°C, samples were then cured 150°C/1 hr + 177°C/2 hrs + 204°C/24 hrs.

Table 13

Moisture Absorption of Cured Resins<sup>1</sup>

Resin System	After 24 hrs at RT in Water, wt%	Saturation at 60°C, 95% RH Wt%	After 72 hrs Water Boil Wt%
C-2	0.20	0.83	3.20
IME-9	0.22	0.75	2.22
-10	0.24	0.48	2.07
-11	-	-	2.72
-11-3	0.17	0.00	2.01
-11-D	0.49	0.50	2.23
-12	-	-	-
-12-3	0.22	0.30	1.94
-12-D	0.30	0.95	2.10
-13	0.35	0.61	2.39
-14	0.34	0.65	2.83
-15	0.39	0.80	4.02
-16	0.54	0.90	5.35
3501-6	0.40	-	3.33

<sup>1</sup>See Table 11 for exact cure cycle. Except for resin C-2, samples were compression molded at 0.69 to 3.45 MPa pressure, depending on resin system. Pressure was applied at about 150°C, samples were then cured 150°C/1 hr + 177°C/2 hrs + 204°C/24 hrs.

Table 14

Cured Resin Thermal Properties<sup>1</sup>

Resin System	DSC Transitions, °C		TMA Tg °C	TGA Wt% Loss 300°C	% Char TGA Method <sup>3</sup>
	Endothermic	Exothermic			
Control resin C-2	230	350,390,500	222	0.5	20
IME-9	225	400>480	197	0	38
-10	210	350>480	200	0	37
-11	100,220	>360 <sup>2</sup>	97, 219	0	19
-11-3	-	360 <sup>2</sup>	82	5	17
-11D	200	>360 <sup>2</sup>	149	5	42
-12	100,220	>360 <sup>2</sup>	210	0	32
-12-3	90,165,230	380>400	85, 120	2	22
-12D	200	>360 <sup>2</sup>	106, 160	2.5	33
-13	200,310	375,500	217	0	40
-14	200,225	375,480	212	1.0	39
-15	225,325	400,500	180	0.5	35
-16	225	350,480	216		40
Hercules 3501-6 epoxy resin	-	-	~180	1.0	15

<sup>1</sup> See Table 11 for exact cure cycle. Except for resin C-2, samples were compression molded at 0.69 to 3.45 MPa pressure, depending on resin system. Pressure was applied at about 150°C, samples were then cured 150°C/1 hr + 177°C/2 hrs + 204°C/24 hrs

<sup>2</sup> Stopped DSC at this temperature

<sup>3</sup> In nitrogen, % residue up to 800°C

Table 15  
Tensile Properties<sup>1</sup> of IME Resins

Resin System	Strength		Modulus		Strain to Failure %
	psi	MPa	10 <sup>6</sup> psi	GPa	
Control resin C-2	2710	18.7	0.59	4.07	0.54
IME-10	5230	36.0	0.54	3.72	0.83
-11-3	4600	31.7	0.61	4.24	1.20
-12	5480	37.8	0.28	1.93	2.20
-12-3	5540	38.2	0.37	2.55	1.22
-13	2900	20.0	0.60	4.14	0.50
-14	2500	17.2	0.57	3.93	0.45
-16	2420	16.7	0.54	3.72	0.49

<sup>1</sup> See Table 11 for exact cure cycle. Except for resin C-2, samples were compression molded at 0.69 to 3.45 MPa pressure, depending on resin system. Pressure was applied at about 150°C, samples were then cured 150°C/1 hr + 177°C/2 hrs + 204°C/24 hrs

Table 16

Compression Properties of IME Resins<sup>1</sup>

Resin System	Strength		Modulus	
	ksi	MPa	10 <sup>6</sup> psi	GPa
Control C-2	33.6	231	0.64	4.41
IME-9	19.0	131	0.49	3.38
-10	39.2	270	0.69	4.76
-11-D	12.0	82.7	0.79	5.45
-11-3	20.7	143	-	-
-12	29.5	203	0.49	3.38
-12-D	17.9	123	0.57	3.93
-12-3	38.0	262	0.66	4.55
-13	29.8	206	0.71	4.89
-14	31.0	214	-	-
-15	29.8	206	0.69	4.79
-16	30.5	210	0.67	4.62

<sup>1</sup> See Table 11 for exact cure cycle. Except for resin C-2, samples were compression molded at 0.69 to 3.45 MPa pressure, depending on resin system. Pressure was applied at about 150°C, samples were then cured 150°C/1 hr + 177°C/2 hrs + 204°C/24 hrs



Table 17

Composition of Celion 6000<sup>1</sup>/IME Resin Composites<sup>2</sup>

10° off axis

14.0 cm x 25.4 cm x 0.139 cm (5 ply)

<u>Composite No.</u> <sup>3,4</sup>	<u>Resin Components</u>	<u>Total Wt, g</u>	<u>Component Wt, g</u>
Control C-2-2B	MY720/3,3'-DDS	25.9	17.26/8.63
C-IME-9-2B	MY720/6F-3,3'-DDS (NASA 159A)	26.1	9.29/16.81
C-IME-10-2-B	MY720/6F-3,3'-DDS (NASA 159A) 3,3'-DDS	26.1	12.14/11.5/3.00
C-IME-18-1	MY720/6F-3,3'-DDS-1,12-DDA (Method B, NASA 144B)	26.1	9.60/16.48
C-IME-11-D	MY720/6F-3,3'-DDS-1,12-DDA (Method D, NASA 302)	22.8	9.6/13.2
C-IME-12-D	MY720/6F-3,3'-DDS-1,12-DDA (Method D, NASA 302/3,3'-DDS)	24.5	12.42/8.5/3.55
C-IME-13-2	MY720/Gly 200/6F-3,3'-DDS-4,4'-DDS (NASA 173)	26.1	16.80/4.33/4.85
C-IME-14-2	MY720/Gly 100/6F-3,3'-DDS-4,4'-DDS (NASA 173)	26.1	18.53/2.22/4.99
C-IME-15-2	MY720/Gly 200/6F-4,4'-DDS (NASA 120)	26.1	16.80/4.33/4.85
C-IME-16-2	MY720/Gly 100/6F-4,4'-DDS (NASA 120)	26.1	18.53/2.22/4.99

<sup>1</sup>Contains about 42.8g graphite fiber<sup>2</sup>This is the resin weight for 137 cm (54") long tape, but 127 cm (50") used, 5 plies<sup>3</sup>Resin dissolved in MEK (minimum quantity) and brushed onto the fiber; tape<sup>4</sup>dried at RT, then 60°C, vacuum, 1 hr<sup>4</sup>Cured as described in Table 18

Table 18

Celion 6000/IME Resin Composites  
Compression Molded

<u>Composite No.</u>	<u>Processing Parameters</u>
C-2-B	RT→150°C, contact P (3.9°C/min), then at 150°C (gelation); application of pressure (1.38 MPa) to STOPS, hold 1 hr, then 150°C→177°C (2.1°C/min), hold 177°C/2 hrs (1.38 MPa), postcure 204°C/24 hrs, air circulating oven
C-IME-9-2B	RT→150°C, contact P (3.2°C/min), then at 150°C (gelation) application of pressure (1.38 MPa) to STOPS, hold 1 hr, then 150°C→177°C (2.2°C/min), hold 177°C/2 hrs (1.38 MPa), postcure 204°C/24 hrs air circulating oven
C-IME-10-2B	RT→150°C, contact P (3.2°C/min), then at 150°C, application of pressure (3.45 MPa) to STOPS, hold 1 hr, 150°C→177°C (1.6°C/min), hold 177°C/2 hrs (3.45 MPa), postcure 204°C/24 hrs, air circulating oven
C-IME-11-D	RT→150°C, apply 1.38 MPa initially, at 150°C apply 3.45 MPa (hold 1 hr), then 150°C→177°C (2.2°C/min), hold 177°C/2 hrs (3.45 MPa), postcure 204°C/24 hrs
C-IME-12-D	Same as C-IME-11-3A
C-IME-13-2	RT→150°C, contact P (20°C/min), then at 150°C (gelation) application pressure (3.45 MPa), hold 150°C/1 hr (3.45 MPa) 150°C→177°C (3.45 MPa), hold 2 hrs, then postcure 204°C/24 hrs
C-IME-14-2	Same as C-IME-13-2
C-IME-15-2	Same as C-IME-13-2
C-IME-16-2	Same as C-IME-13-2
C-IME-18-1	Same as C-IME-11-34 except applied 6.9 MPa and held throughout

Table 19

Composition data for Compression Molded  
Celion 6000/IME Composites

(5 ply 10° off-axis composites)

<u>Composite Number</u>	<u>Density g/cc</u>	<u>Calculated Vol %</u>		<u>Composite Ply Thickness mm/ply</u>
		<u>Resin</u>	<u>Fiber</u>	
Control C-2B	1.56	44	56	0.279
C-IME-9-2B	1.55	45	55	0.305
-10-2B	1.56	37	63	0.305
-11-3A	1.50	46	54	0.309
-12-3A	1.54	43	57	0.295
-13-2	1.56	45	55	0.305
-14-2	1.54	43	57	0.295
-15-2	1.56	38	62	0.272
-16-2	1.54	36	64	0.263
-18-1	1.55	45	55	0.314

Table 20

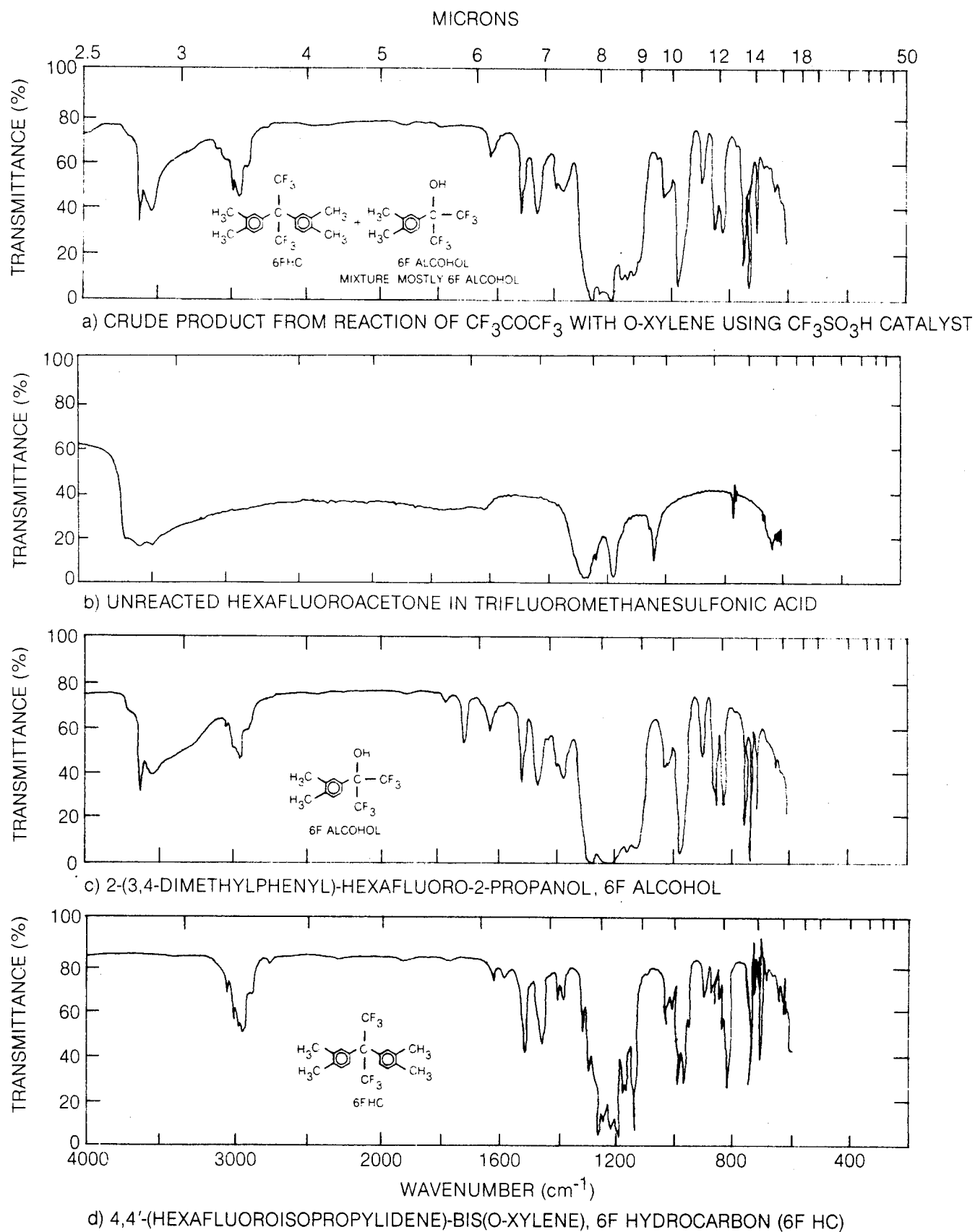
## Tensile Properties of 10° Off-Axis Celion 6000/IME Composites

Composite No.	Resin Formulation	Tensile Properties				Intralaminar Shear Properties				Composite <sup>1</sup> Intralaminar Shear Strain to Failure $\epsilon_{112}$ , %	Shear Strain-Failure in Resin %
		Strength		Modulus	Strength		Modulus				
		ksi	MPa	10 <sup>6</sup> psi	GPa	ksi	MPa	10 <sup>6</sup> psi	GPa		
C-2-2B (control)	MY720/3, 3'-DDS	45.8	316	12.3	84.8	7.84	54.0	1.13	7.79	1.08	4.65
C-IME-9-2B	MY720/6F-3, 3'-DDS	62.8	433	11.6	80.0	10.7	73.8	1.09	7.52	1.93	10.6
C-IME-10-2B	MY720/6F-3, 3'-DDS/3, 3'-DDS	55.8	454	12.3	88.3	11.2	77.2	1.05	7.24	1.79	9.07
C-IME-18-1	MY720/3, 3'-DDS-1, 12-DDA (Method B)	56.2	387	10.5	72.4	9.61	66.3	0.99	6.82	1.71	9.56
C-IME-11-D	MY720/6F-3, 3'-DDS-1, 12-DDA (Method D)	39.8	274	10.7	73.8	6.80	46.8	0.90	6.20	1.51	6.80
C-IME-12-D	MY720/6F-3, 3'-DDS-1, 12-DDA (Method D)/3, 3'-DDS	24.1	166	13.1	90.3	4.12	28.4	0.89	6.14	0.90	3.73
C-IME-13-2	MY720/Gly200/6F-3, 3'-DDS-4, 4'-DDS	56.7	391	13.9	95.8	9.69	66.8	1.18	8.14	1.35	6.15
C-IME-14-2	MY720/Gly100/6F-3, 3'-DDS-4, 4'-DDS	60.3	416	12.0	82.8	10.3	71.0	1.18	8.14	1.36	6.53
C-IME-15-2	MY720/Gly200/6F-4, 4'-DDS	38.1	263	13.6	93.8	6.52	44.9	1.10	7.59	0.75	3.60
C-IME-16-2	MY720/Gly100/6F-4, 4'-DDS	49.6	342	12.0	82.8	8.48	58.5	1.10	7.59	1.20	6.08

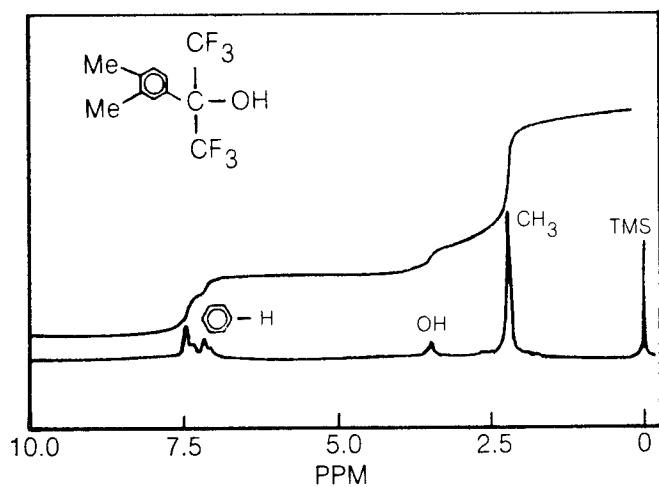
<sup>1</sup> strain gaged with a rectangular rosette of 0°, 45° and 90° gages (type EA-06-062RB-120)

# INFRARED SPECTRA OF FLUORINATED INTERMEDIATES

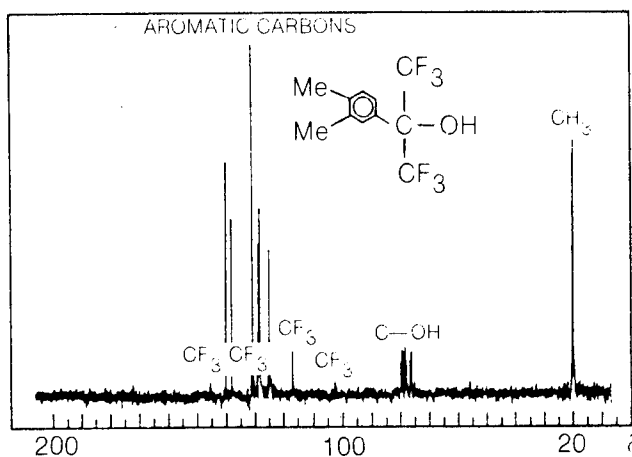
FIG. 1



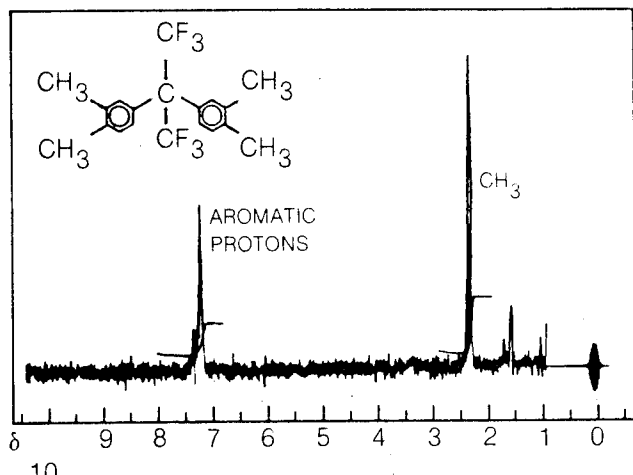
## NMR SPECTRA OF FLUORINATED COMPOUNDS



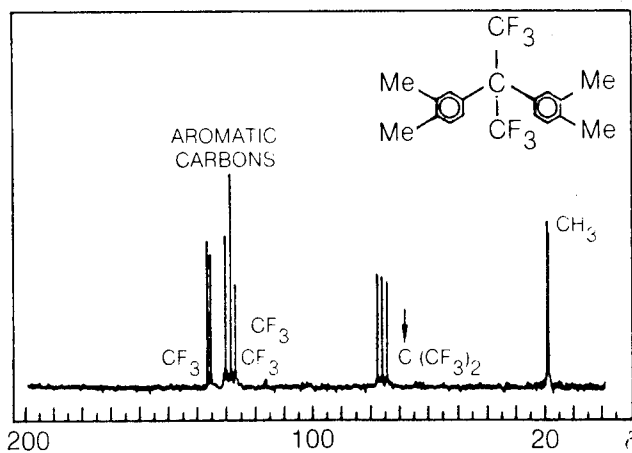
a) PROTON NMR OF  
2-(3,4-DIMETHYLPHENYL)-1,2-HEXAFLUORO-2-PROPANOL



b) <sup>13</sup>C NMR OF  
2-(3,4-DIMETHYLPHENYL)-1,2-HEXAFLUORO-2-PROPANO.

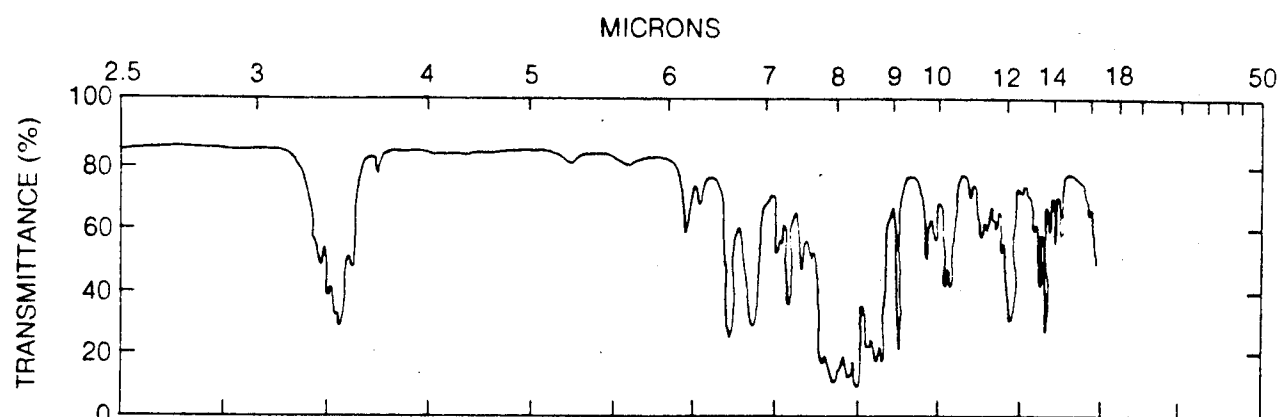


c) PROTON NMR OF  
4,4'-(HEXAFLUOROISOPROPYLIDENE) BIS(O-XYLENE)

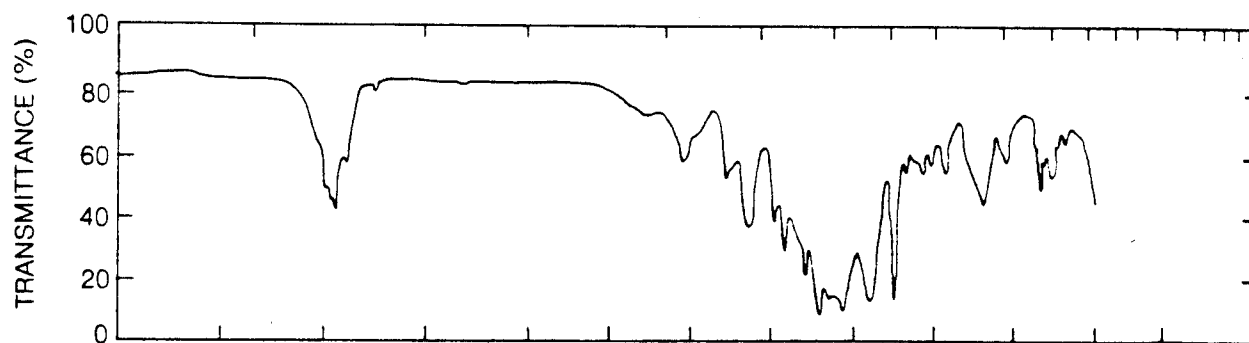


d) <sup>13</sup>C NMR OF 4,4'-(HEXAFLUOROISOPROPYLIDENE)  
BIS(O-XYLENE)

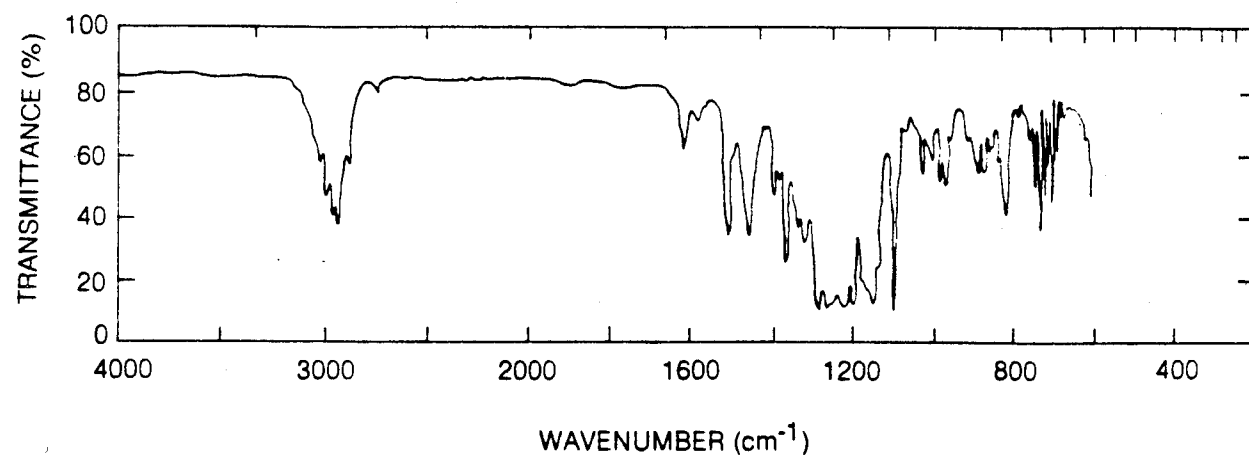
## INFRARED SPECTRA OF FLUORINATED INTERMEDIATES



a) FLUORINATED HYDROCARBON SIMILAR TO 6F HC (N203E-3)

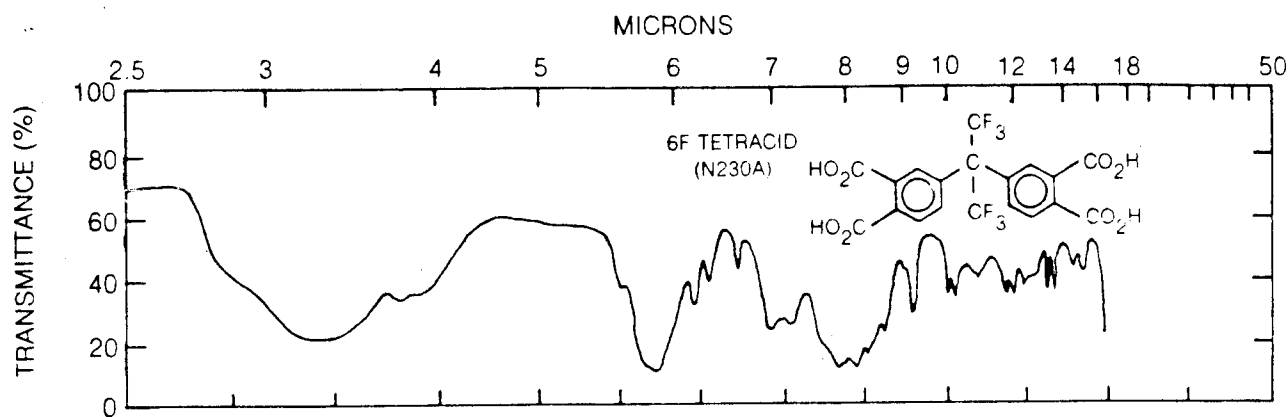
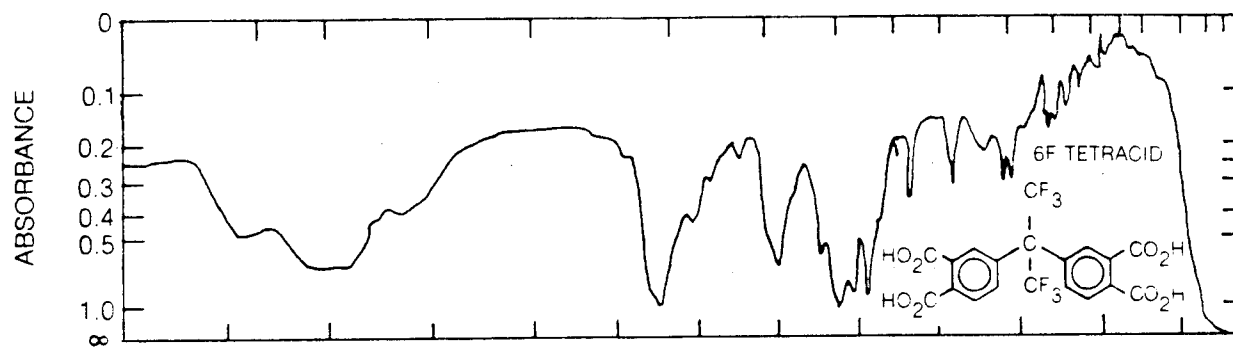


b) FLUORINATED HYDROCARBON SIMILAR TO 6F HC (N212D6)

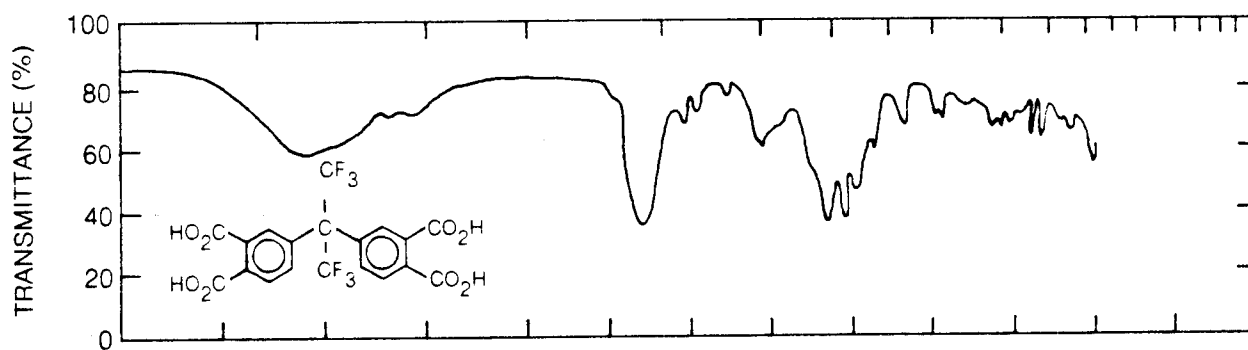
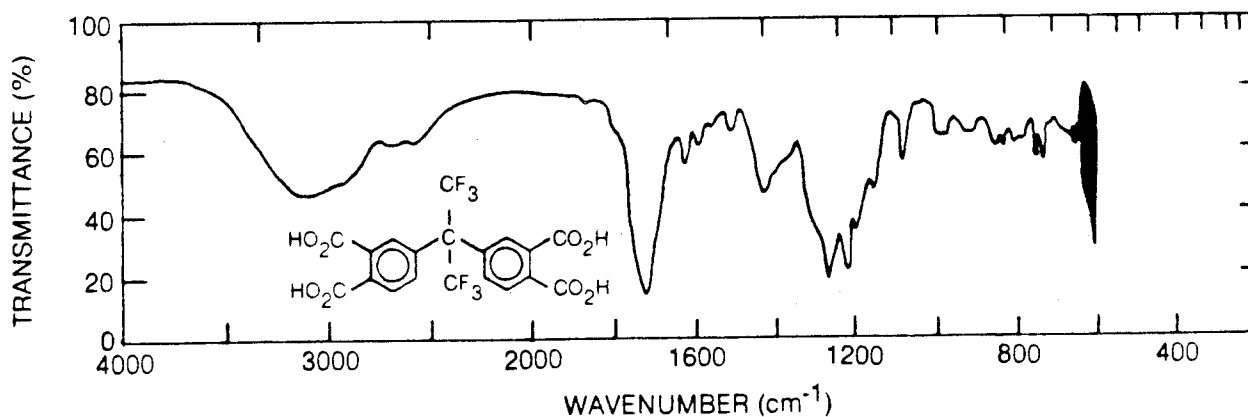


c) FLUORINATED HYDROCARBON SIMILAR TO 6FHC (N212D6H)

## INFRARED SPECTRA OF 6F TETRACID

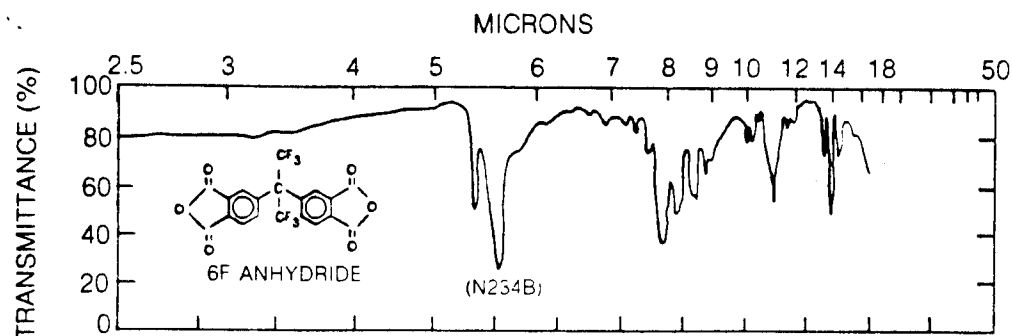
a) 6F TETRACID (N230A) FROM  $\text{KMnO}_4$  OXIDATION OF 6FHC

b) 6F TETRACID (AUTHENTIC SAMPLE)

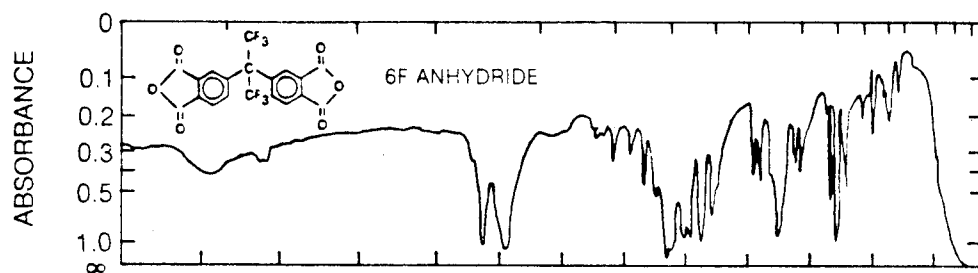
c) 6F TETRACID (N230A) RECRYSTALLIZED FROM  $\text{EtOH/n-HEXANE}$ d) 6F TETRACID (N225A) FROM  $\text{HNO}_3$  OXIDATION OF 6FHC



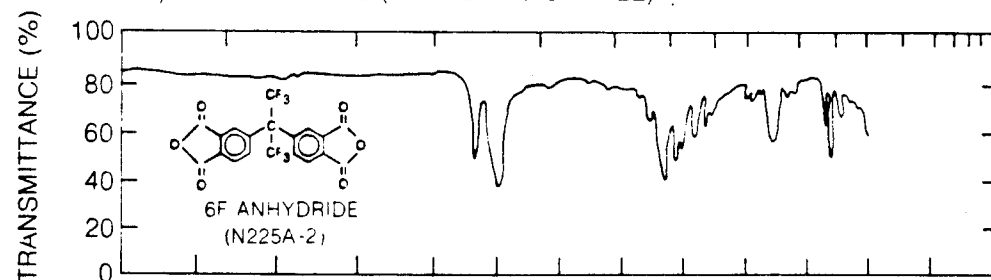
## INFRARED SPECTRA OF 6F ANHYDRIDE



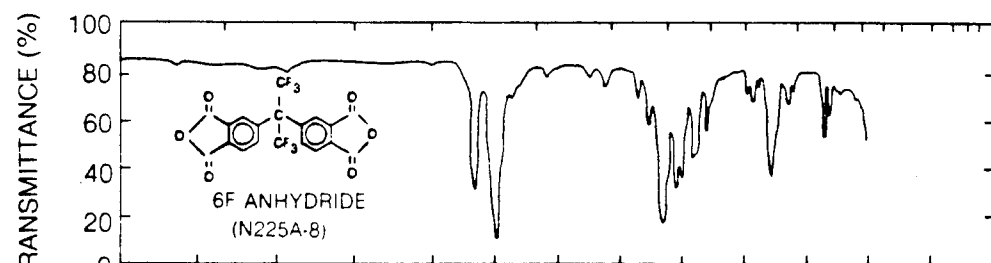
a) 6F ANHYDRIDE (N234B) FROM ACETIC ANHYDRIDE DEHYDRATION OF 6F TETRACID



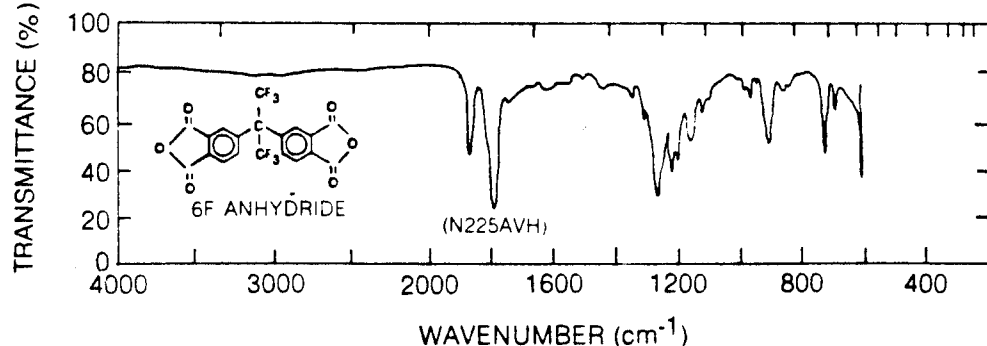
b) 6F ANHYDRIDE (AUTHENTIC SAMPLE)



c) 6F ANHYDRIDE (N225A-2) FROM DEHYDRATION IN TOLUENE

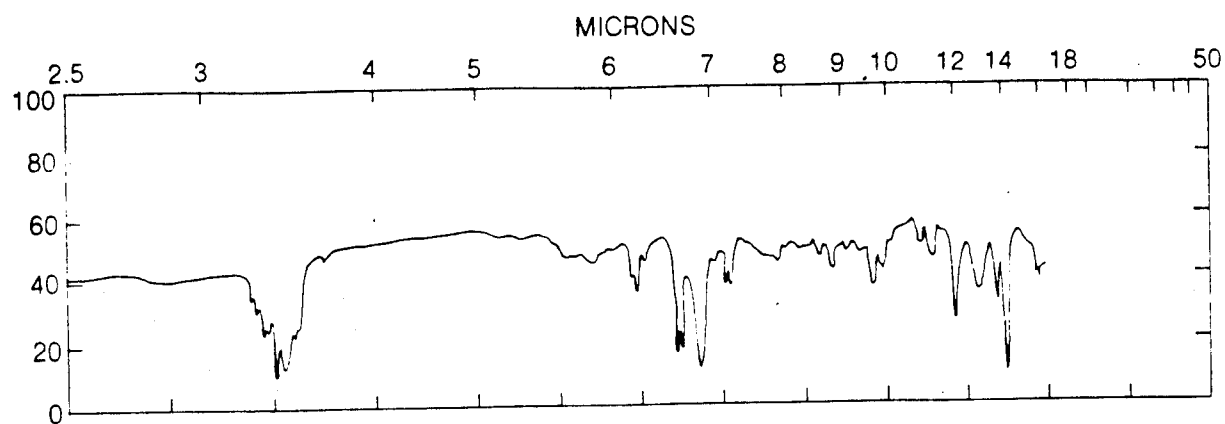


d) 6F ANHYDRIDE (N225A-8) FROM SUBLIMATION OF CRUDE ANHYDRIDE

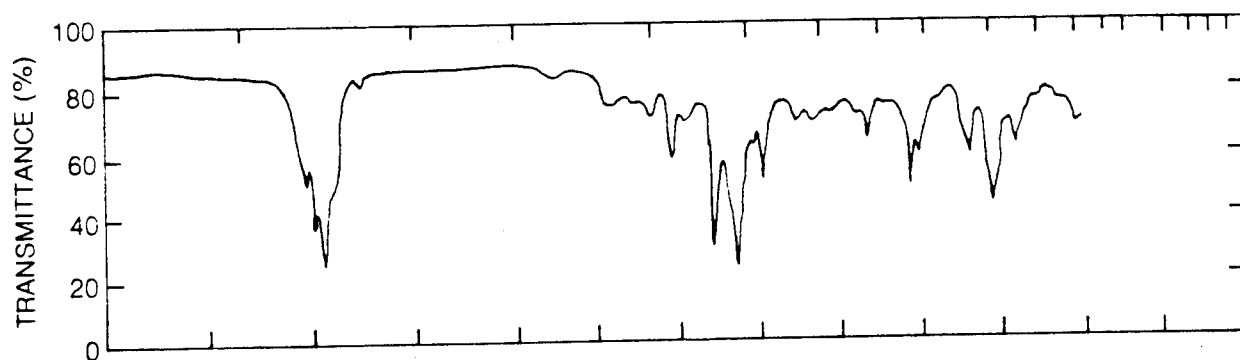


e) 6F ANHYDRIDE (N225AVH) FROM VACUUM HEAT TREATMENT OF 6F TETRACID (N225A)

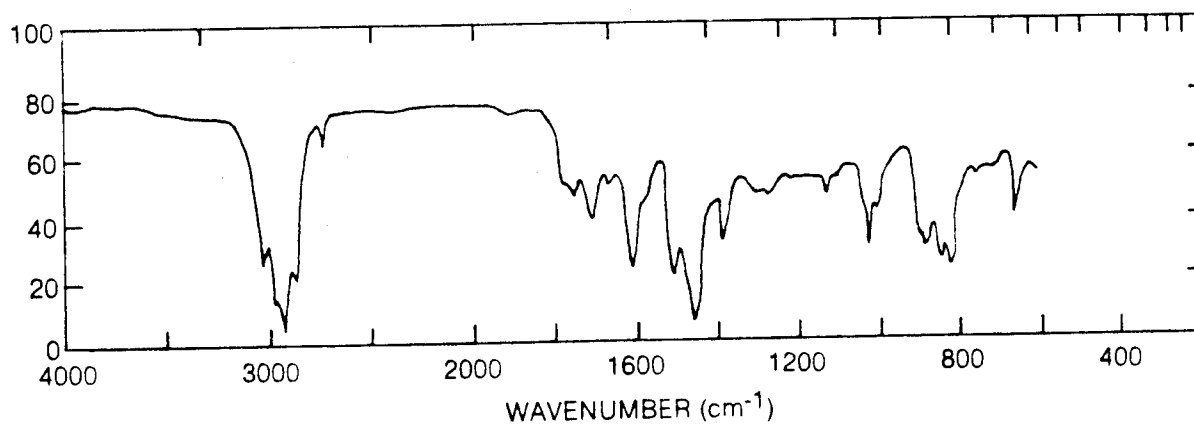
INFRARED SPECTRA OF PRODUCTS FROM REACTION OF  
O-XYLENE WITH HEXACHLOROACETONE



a) CHLORINATED HYDROCARBON (N75B)

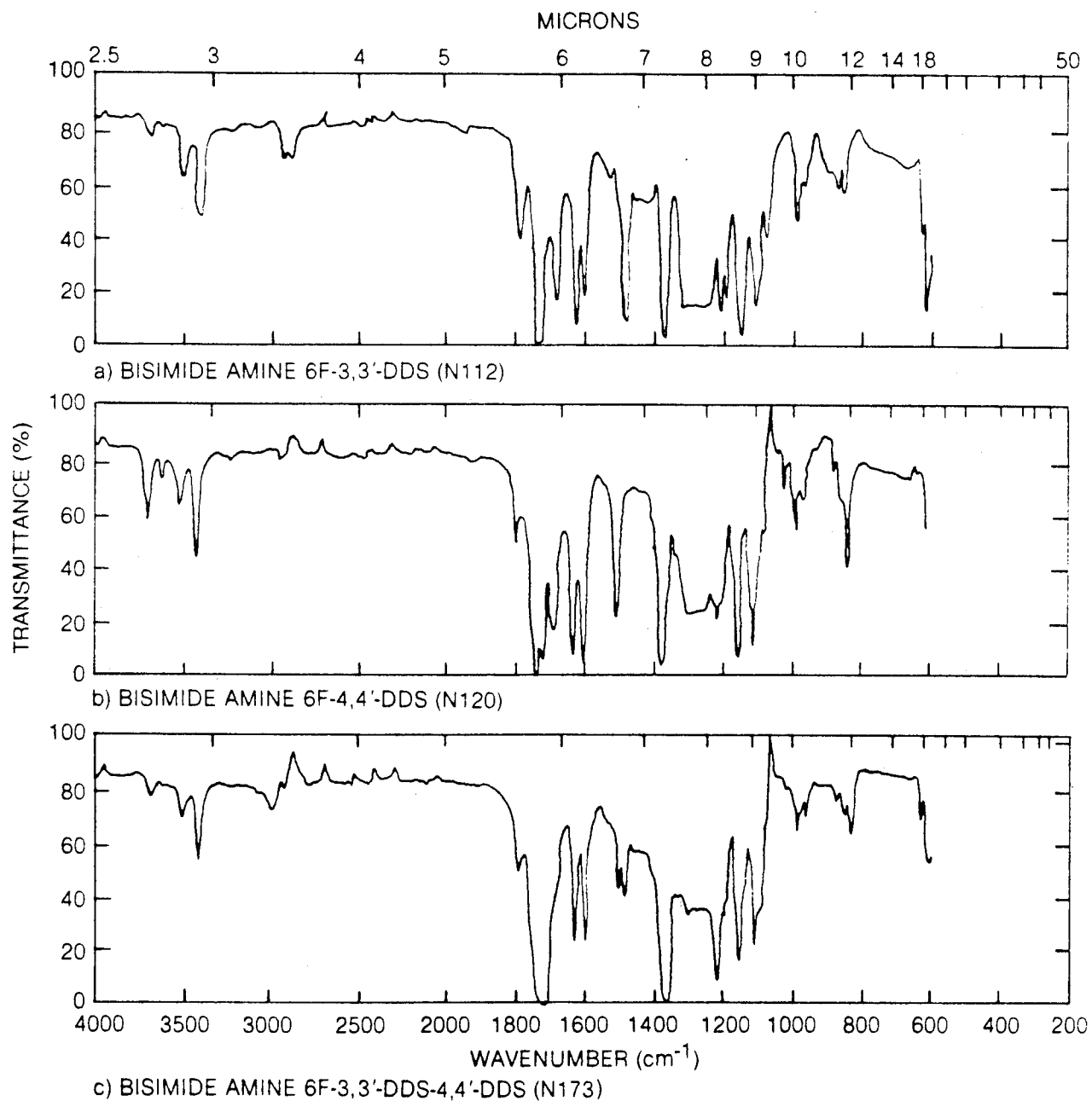


b) CHLORINATED HYDROCARBON (N75-8)

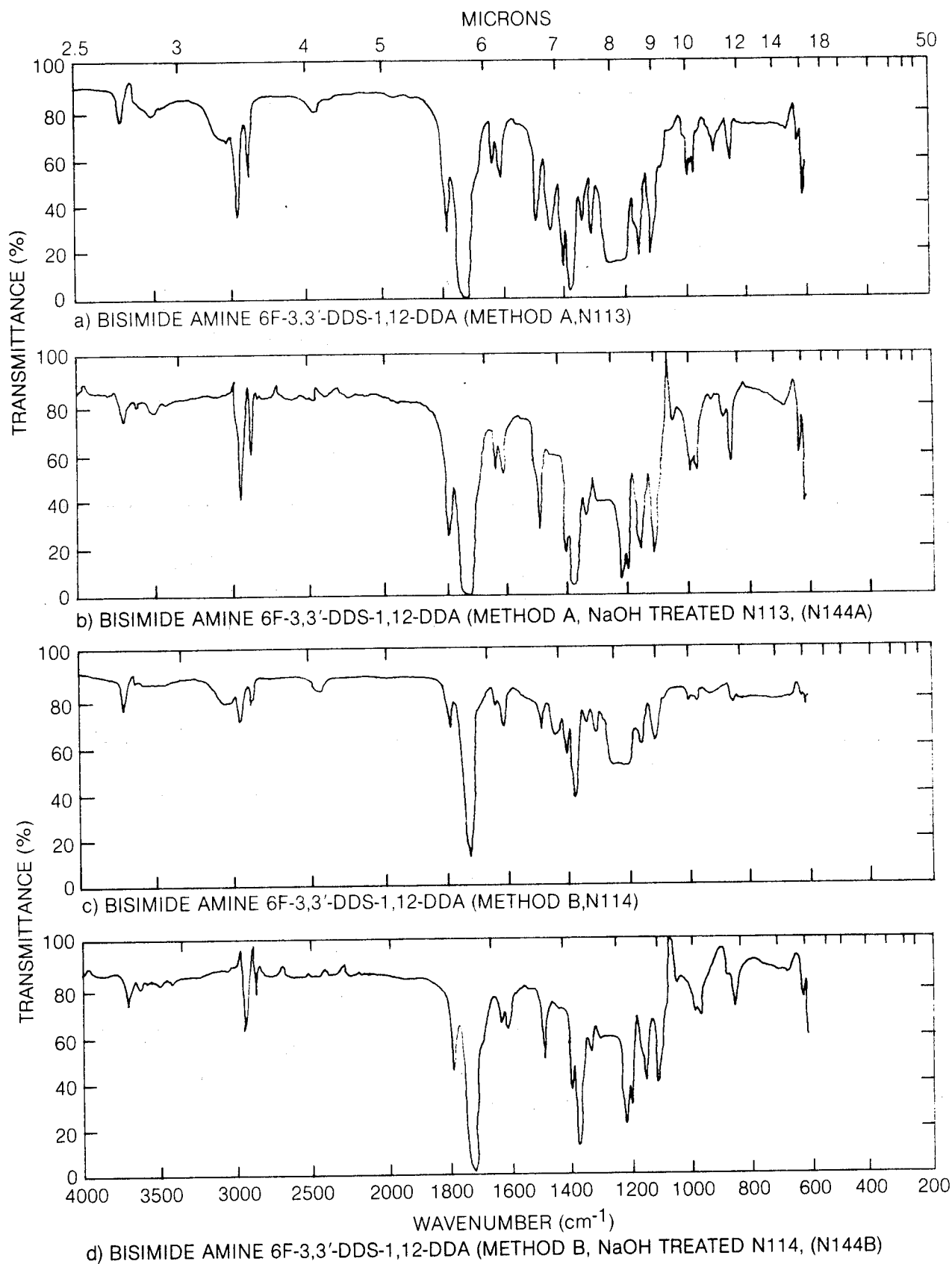


c) CHLORINATED HYDROCARBON (N90-8)

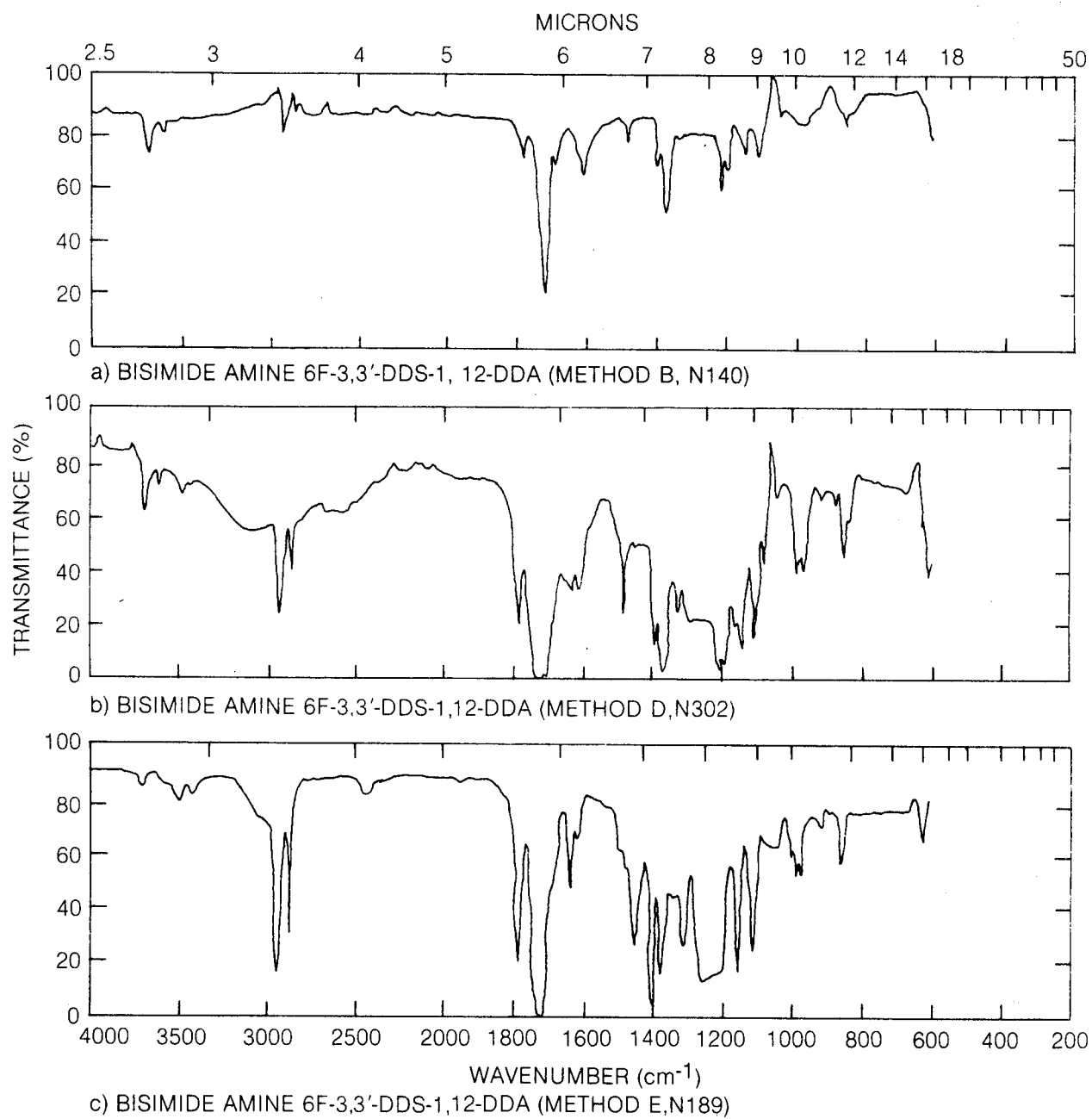
## INFRARED SPECTRA OF BISIMIDE AMINES



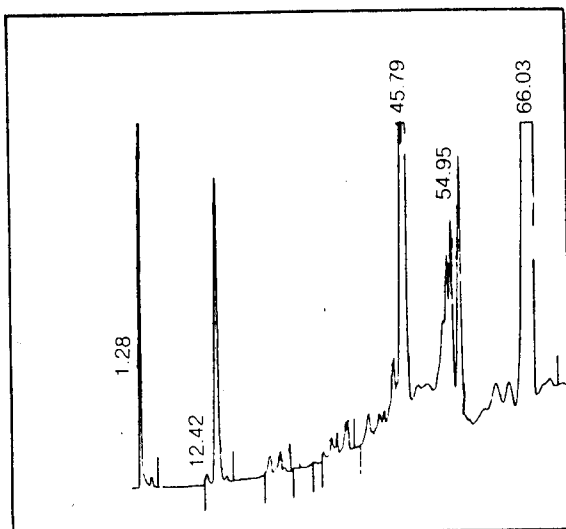
## INFRARED SPECTRA OF BISIMIDE AMINES



## INFRARED SPECTRA OF BISIMIDE AMINES



## HPLC ANALYSIS OF BISIMIDE AMINES



a) BISIMIDE AMINE 6F-3,3'-DDS (N112)

## CONDITIONS

COLUMN:  $\mu$  BONDAPAK C<sub>18</sub>SAMPLE SIZE: 20  $\mu$ l

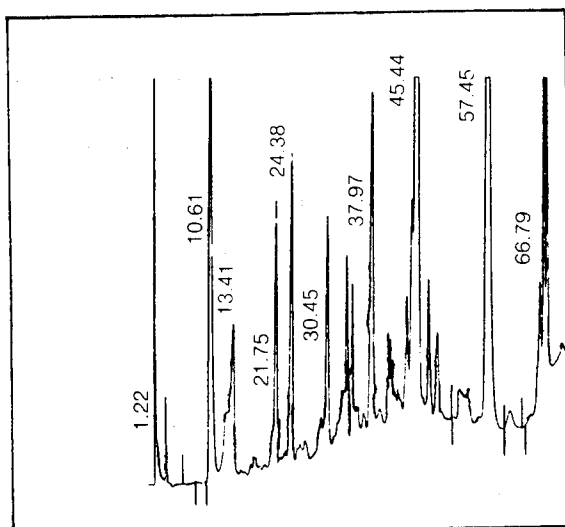
ATTENUATION: UV 1.0 (254 WAVENUMBERS)

CHART SPEED: 0.25 cm/min

INSTRUMENT: WATERS MODEL ALC/GPC 244

## PROGRAM

TOTAL TIME, min	FLOW cc/min	% THF	% H <sub>2</sub> O	CURVE
INITIAL	1.20	20	80	—
2.00	1.20	20	80	6
45.00	1.20	60	40	6
60.00	1.20	100	0	6
65.00	1.20	100	0	6
85.00	1.20	100	0	6
90.00	1.20	20	80	6



b) BISIMIDE AMINE 6F-4,4'-DDS (N120)

## CONDITIONS

COLUMN:  $\mu$  BONDAPAK C<sub>18</sub>SAMPLE SIZE: 20  $\mu$ l

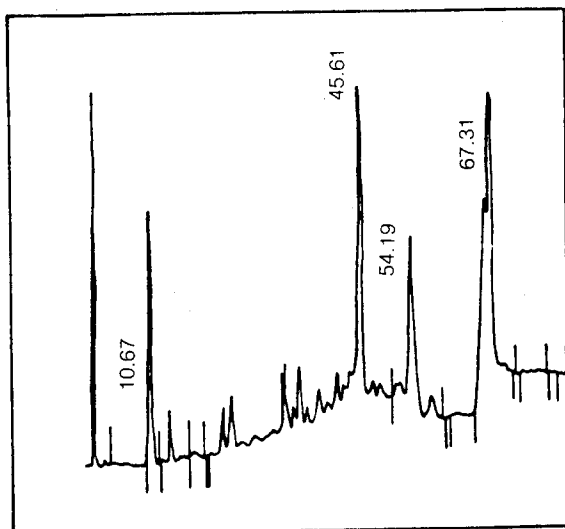
ATTENUATION: UV 1.0 (254 WAVENUMBERS)

CHART SPEED: 0.25 cm/min

INSTRUMENT: WATERS MODEL ALC/GPC 244

## PROGRAM

TOTAL TIME, min	FLOW cc/min	% THF	% H <sub>2</sub> O	CURVE
INITIAL	1.20	20	80	—
2.00	1.20	20	80	6
45.00	1.20	60	40	6
60.00	1.20	100	0	6
65.00	1.20	100	0	6
85.00	1.20	100	0	6
90.00	1.20	20	80	6



TIME, minutes

c) BISIMIDE AMINE 6F-3,3'-DDS-4,4'-DDS (N173)

## CONDITIONS:

COLUMN:  $\mu$  BONDAPAK C<sub>18</sub>SAMPLE SIZE: 20  $\mu$ l

ATTENUATION: UV 1.0 (254 WAVENUMBERS)

CHART SPEED: 0.25 cm/min

INSTRUMENT: WATERS MODEL ALC/GPC 244

## PROGRAM

TOTAL TIME, min	FLOW cc/min	% THF	% H <sub>2</sub> O	CURVE
INITIAL	1.20	20	80	—
2.00	1.20	20	80	6
45.00	1.20	60	40	6
60.00	1.20	100	0	6
65.00	1.20	100	0	6
85.00	1.20	100	0	6
90.00	1.20	20	80	6

## HPLC ANALYSIS OF BISIMIDE AMINES

## CONDITIONS:

COLUMN:  $\mu$  BONDAPAK C<sub>18</sub>SAMPLE SIZE: 20  $\mu$ l

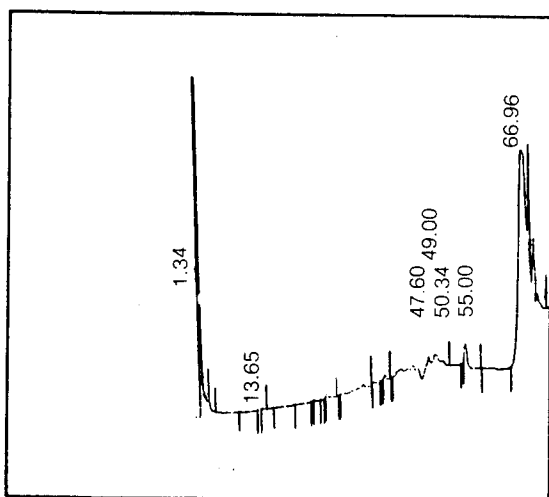
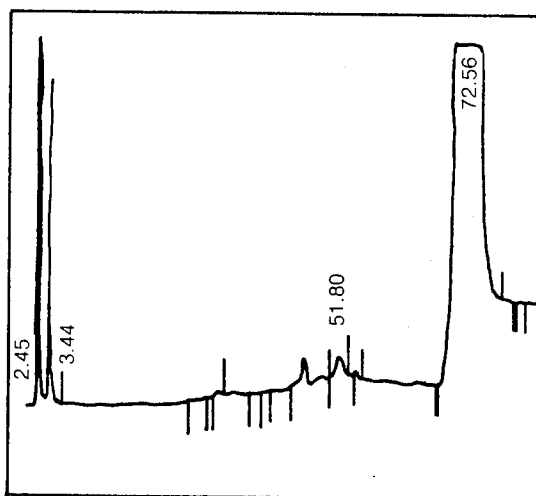
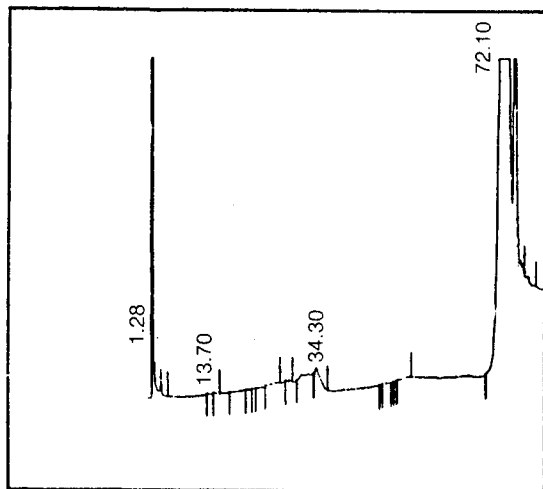
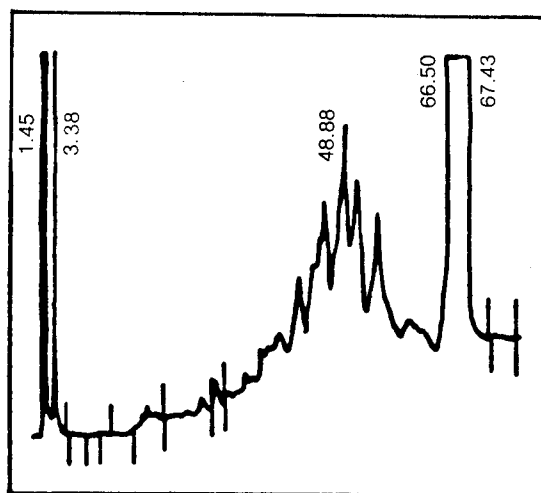
ATTENUATION: UV 1.0 (254 WAVENUMBERS)

CHART SPEED: 0.25 cm/min

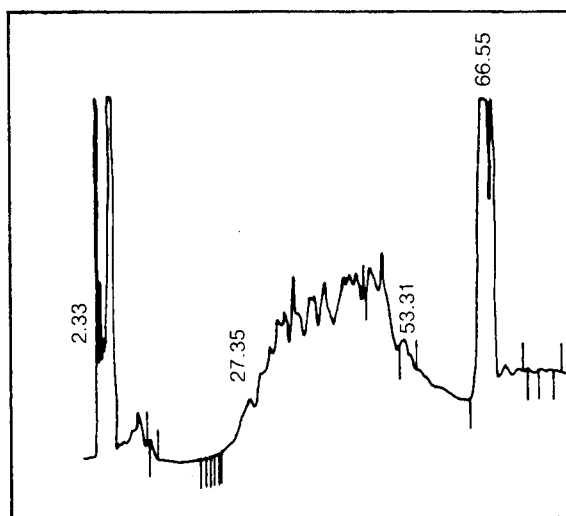
INSTRUMENT: WATERS MODEL ALC/GPC 244

## PROGRAM:

TOTAL TIME, min	FLOW cc/min	% THF	% H <sub>2</sub> O	CURVE
INITIAL	1.20	20	80	—
2.00	1.20	20	80	6
45.00	1.20	60	40	6
60.00	1.20	100	0	6
65.00	1.20	100	0	6
85.00	1.20	100	0	6
90.00	1.20	20	80	6

a) BISIMIDE AMINE 6F-3,3'-DDS-1, 12-DDA  
(METHOD A, N113)b) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA  
(METHOD A, NaOH TREATED N113), N144Ac) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA  
(METHOD B, N114)d) 6F-3,3'-DDS-1,12-DDA  
(METHOD B, NaOH TREATED N114), N144B

## HPLC ANALYSIS OF BISIMIDE AMINES



a) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA (METHOD B, N140)

## CONDITIONS:

COLUMN:  $\mu$  BONDAPAK C<sub>18</sub>SAMPLE SIZE: 20  $\mu$ l

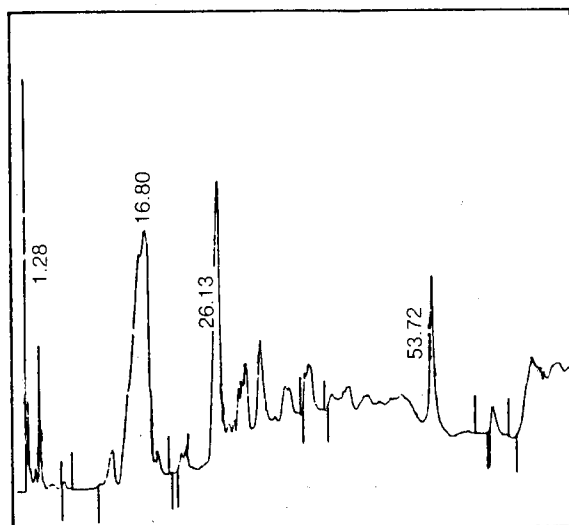
ATTENUATION: UV 1.0 (254 WAVENUMBERS)

CHART SPEED: 0.25 cm/min

INSTRUMENT: WATERS MODEL ALC/GPC 244

## PROGRAM:

TOTAL TIME, min	FLOW cc/min	% THF	% H <sub>2</sub> O	CURVE
INITIAL	1.20	20	80	—
2.00	1.20	20	80	6
45.00	1.20	60	40	6
60.00	1.20	100	0	6
65.00	1.20	100	0	6
85.00	1.20	100	0	6
90.00	1.20	20	80	6



b) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA (METHOD D, N302A)

## CONDITIONS:

COLUMN:  $\mu$  BONDAPAK C<sub>18</sub>SAMPLE SIZE: 20  $\mu$ l

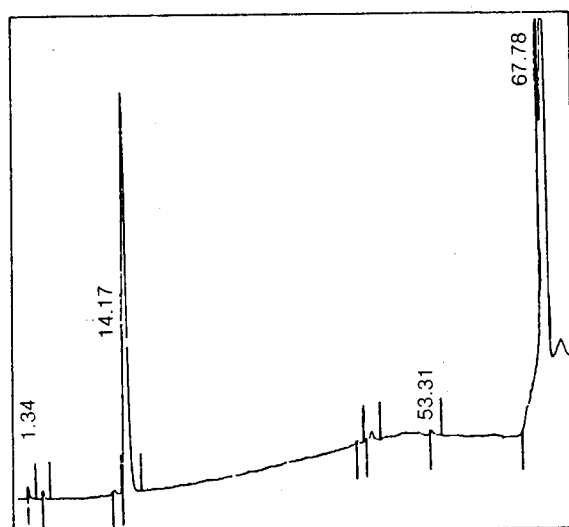
ATTENUATION: UV 1.0 (254 WAVENUMBERS)

CHART SPEED: 0.25 cm/min

INSTRUMENT: WATERS MODEL ALC/GPC 244

## PROGRAM:

TOTAL TIME, min	FLOW cc/min	% THF	% H <sub>2</sub> O	CURVE
INITIAL	1.20	20	80	—
2.00	1.20	20	80	6
45.00	1.20	60	40	6
60.00	1.20	100	0	6
65.00	1.20	100	0	6
85.00	1.20	100	0	6
90.00	1.20	20	80	6



c) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA (METHOD E, N189)

## CONDITIONS:

COLUMN:  $\mu$  BONDAPAK C<sub>18</sub>SAMPLE SIZE: 20  $\mu$ l

ATTENUATION: UV 1.0 (254 WAVENUMBERS)

CHART SPEED: 0.25 cc/min

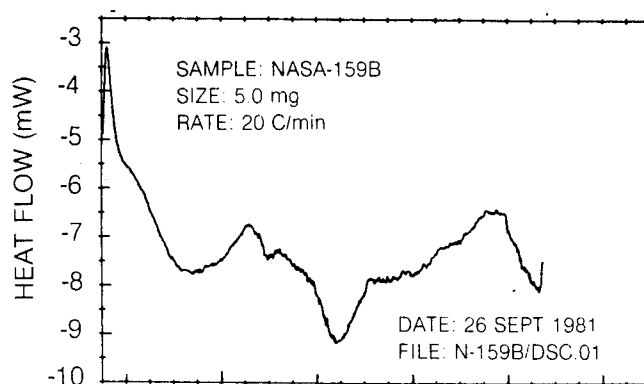
INSTRUMENT: WATERS MODEL ALC/GPC 244

## PROGRAM

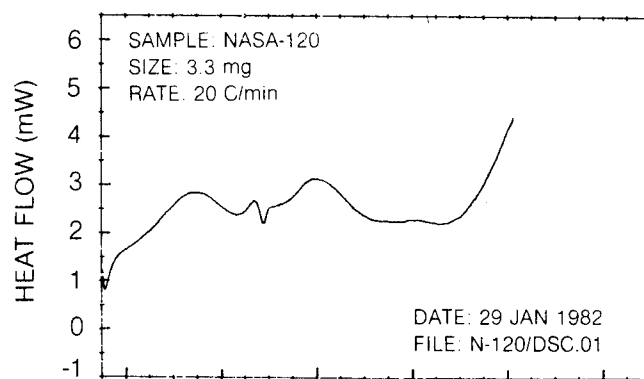
TOTAL TIME, min	FLOW cc/min	% THF	% H <sub>2</sub> O	CURVE
INITIAL	1.20	20	80	—
2.00	1.20	20	80	6
45.00	1.20	60	40	6
60.00	1.20	60	40	6
65.00	1.20	100	0	6
100.00	1.20	100	0	6
115.00	0	100	0	6



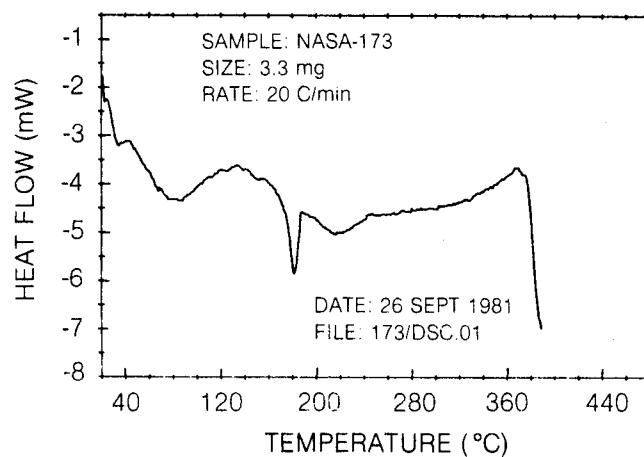
## DSC SCANS OF BISIMIDE AMINES



a) BISIMIDE AMINE 6F-3,3'-DDS (N159B)

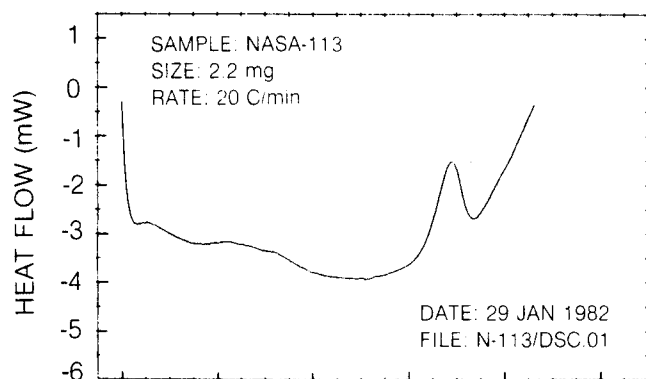


b) BISIMIDE AMINE 6F-4,4'-DDS (N120)

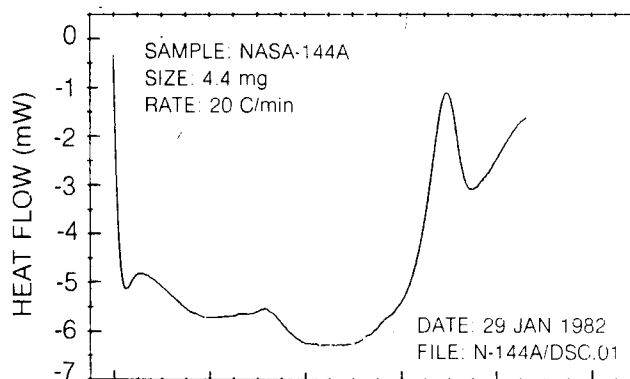


c) BISIMIDE AMINE 6F-3,3'-DDS-4,4'-DDS (N173)

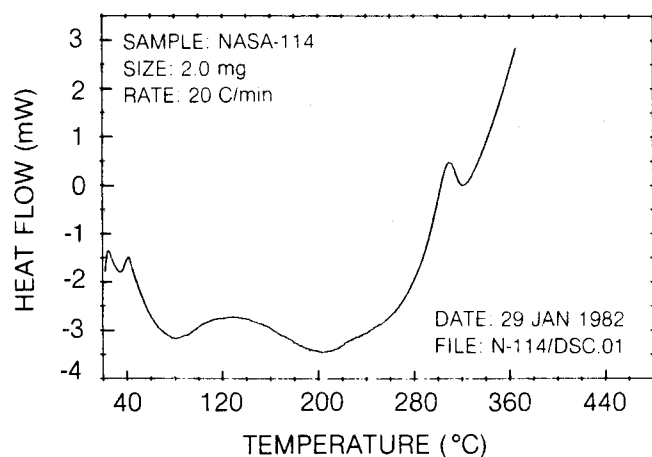
## DSC SCANS OF BISIMIDE AMINES



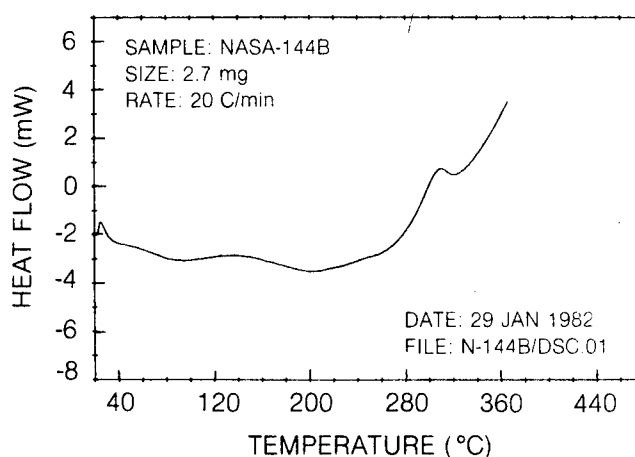
a) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA  
(METHOD A,N113)



b) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA  
(METHOD A, NaOH TREATED N113, (N144A))

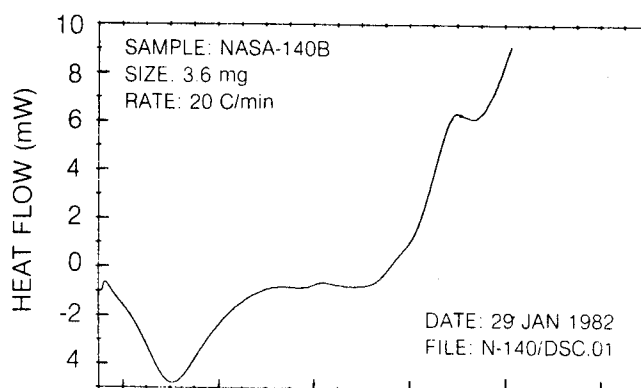


c) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA  
(METHOD B,N114)

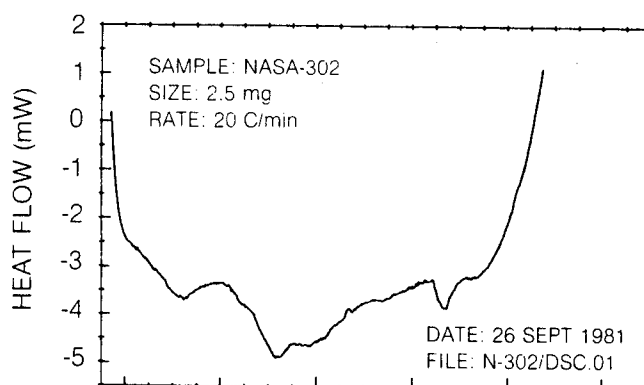


d) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA  
(METHOD B, NaOH TREATED N114, (N144B))

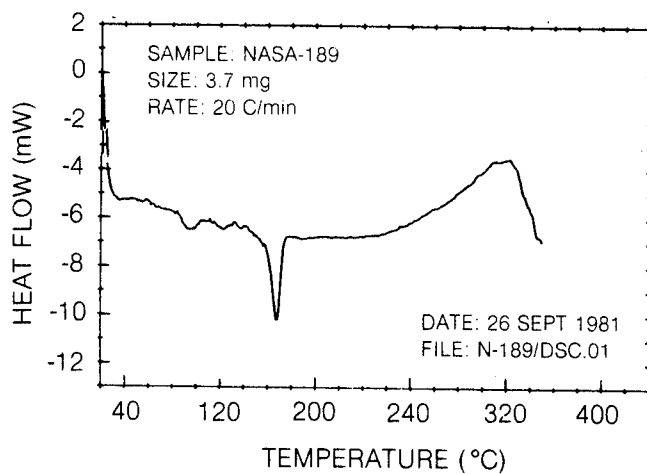
## DSC SCANS OF BISIMIDE AMINES



a) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA  
(METHOD B, N140)

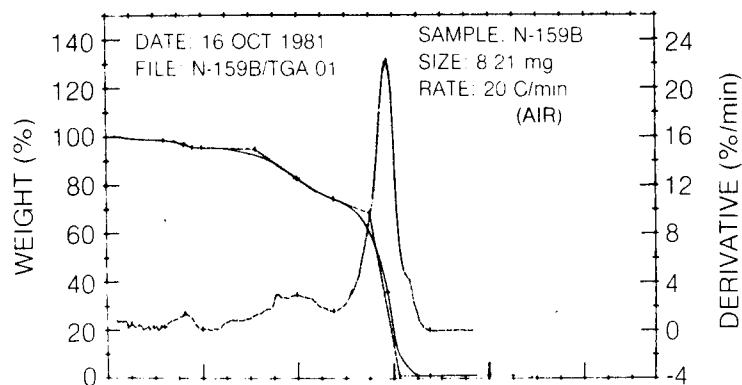


b) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA  
(METHOD D, N302)

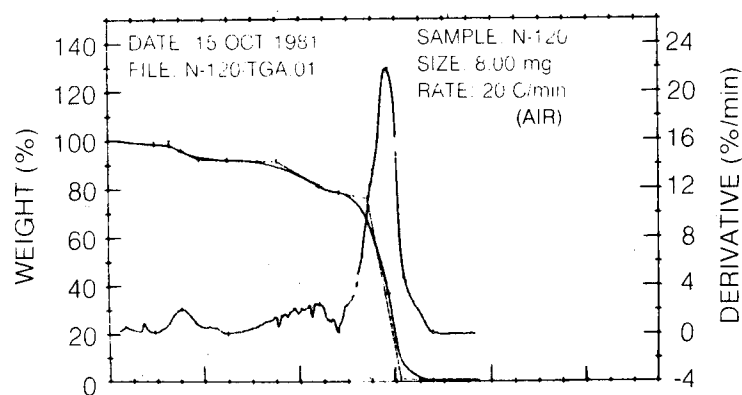


c) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA  
(METHOD E, N189)

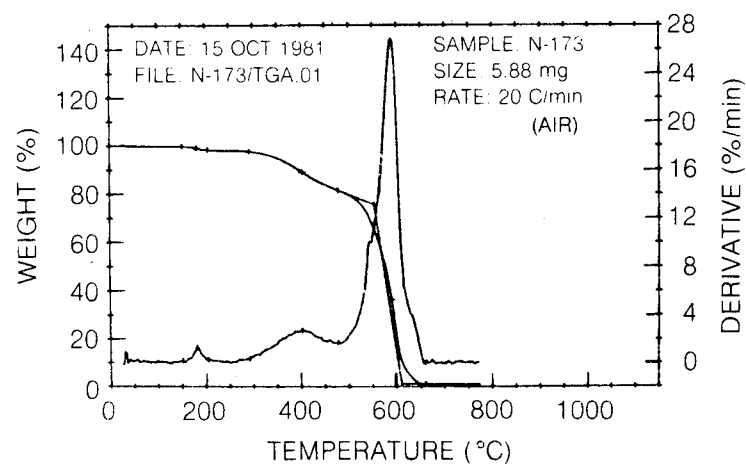
## TGA OF BISIMIDE AMINES



a) BISIMIDE AMINE 6F-3,3'-DDS (N159B)



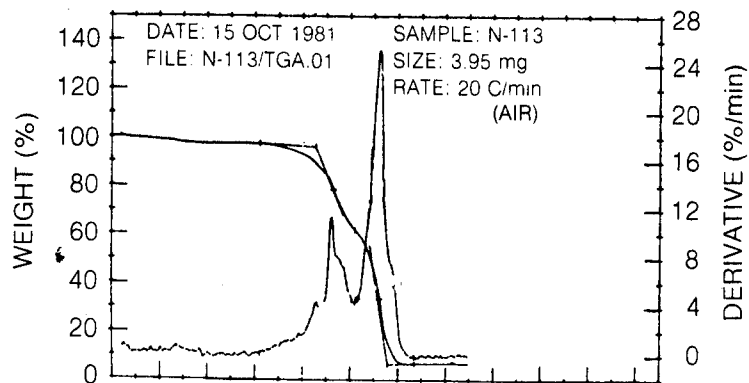
b) BISIMIDE AMINE 6F-4,4'-DDS (N120)



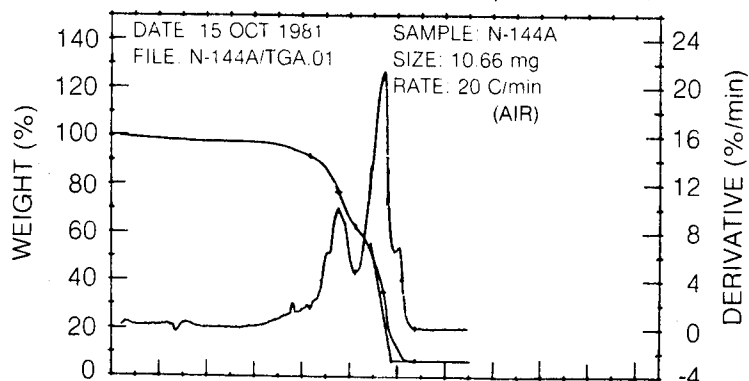
c) BISIMIDE AMINE 6F-3,3'-DDS-4,4'-DDS (N173)

# TGA OF BISIMIDE AMINES

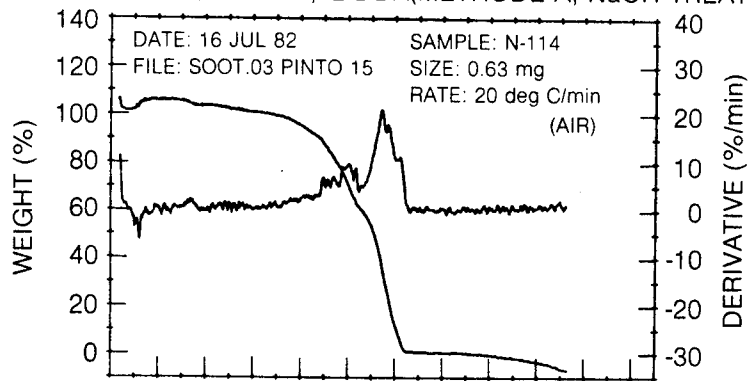
FIG. 17



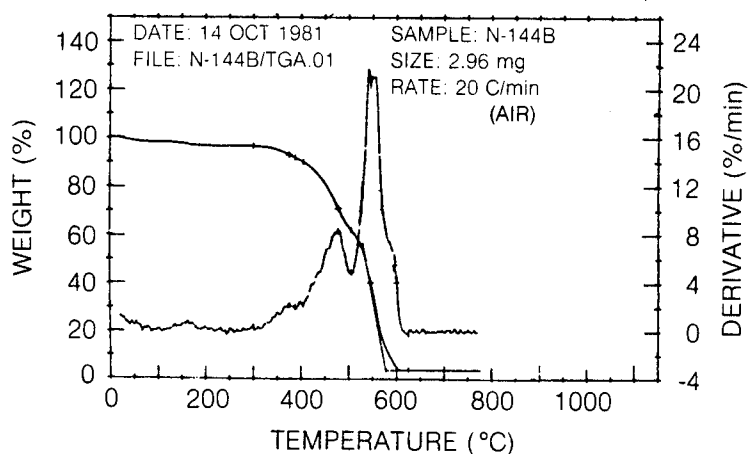
a) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA (METHOD A, N113)



b) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA (METHOD A, NaOH TREATED N113, (N144A))

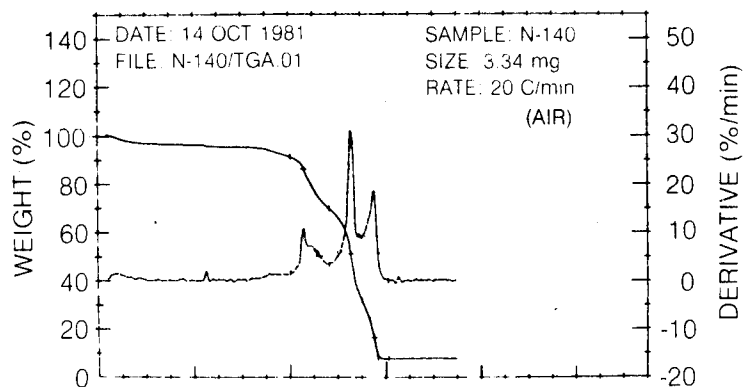


c) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA (METHOD B, N114)

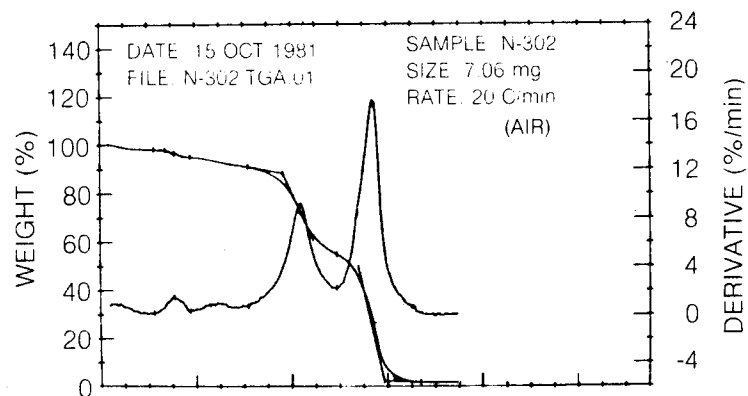


d) 6F-3,3'-DDS-1,12-DDA (METHOD B, NaOH TREATED N114, (N144B))

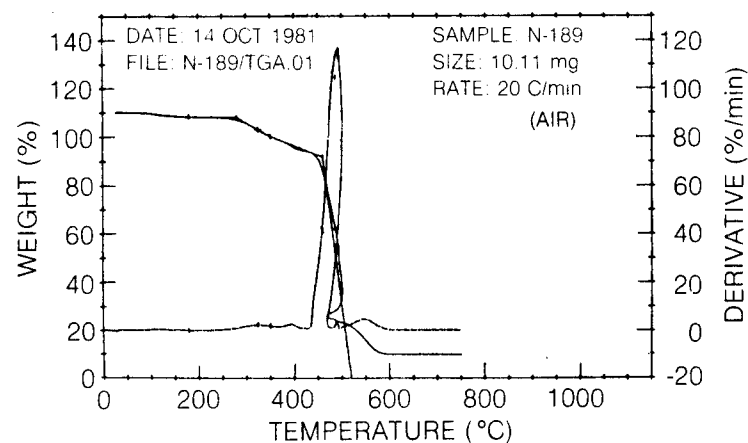
## TGA OF BISIMIDE AMINES



a) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA  
(METHOD B, N140)

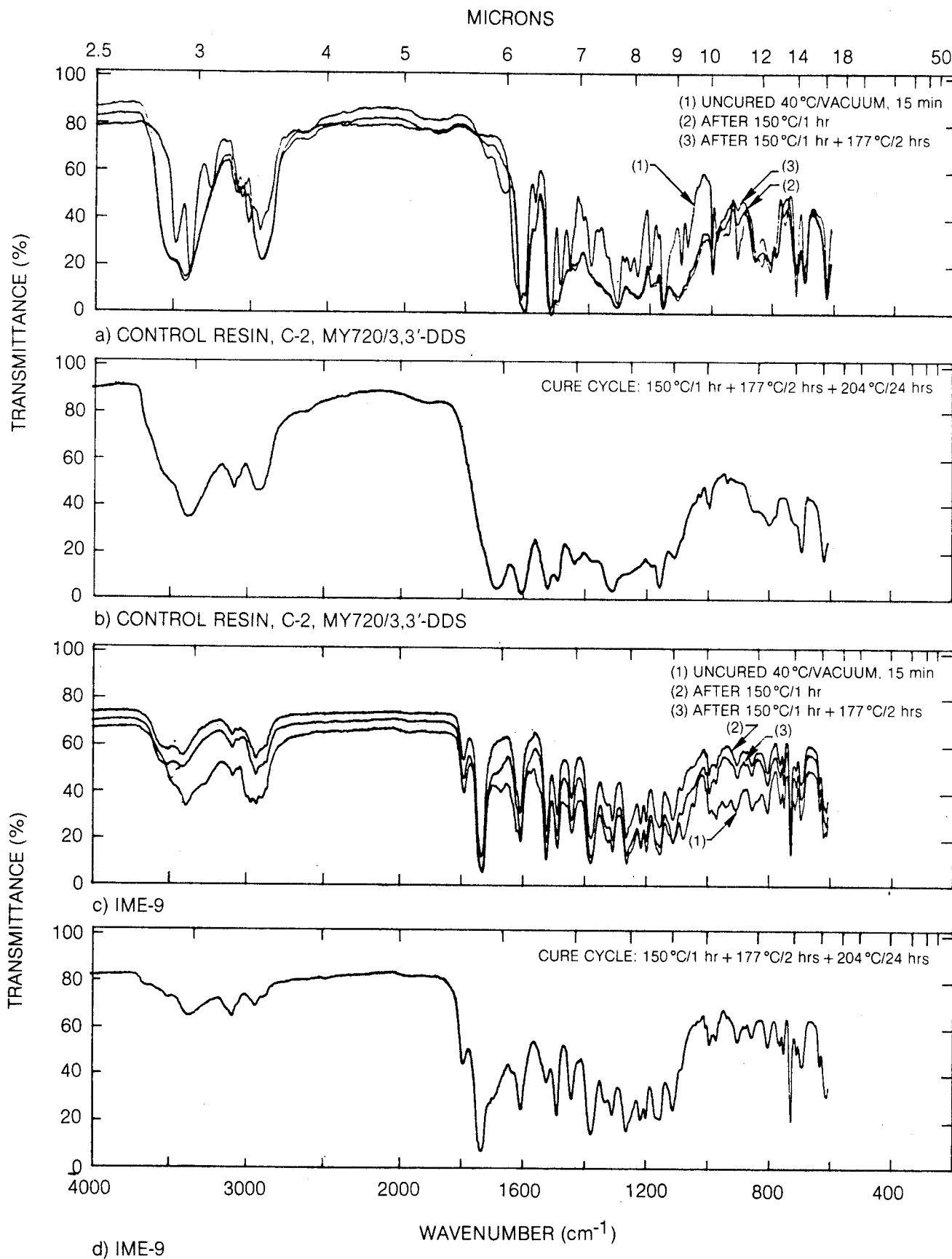


b) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA (METHOD D, N302)

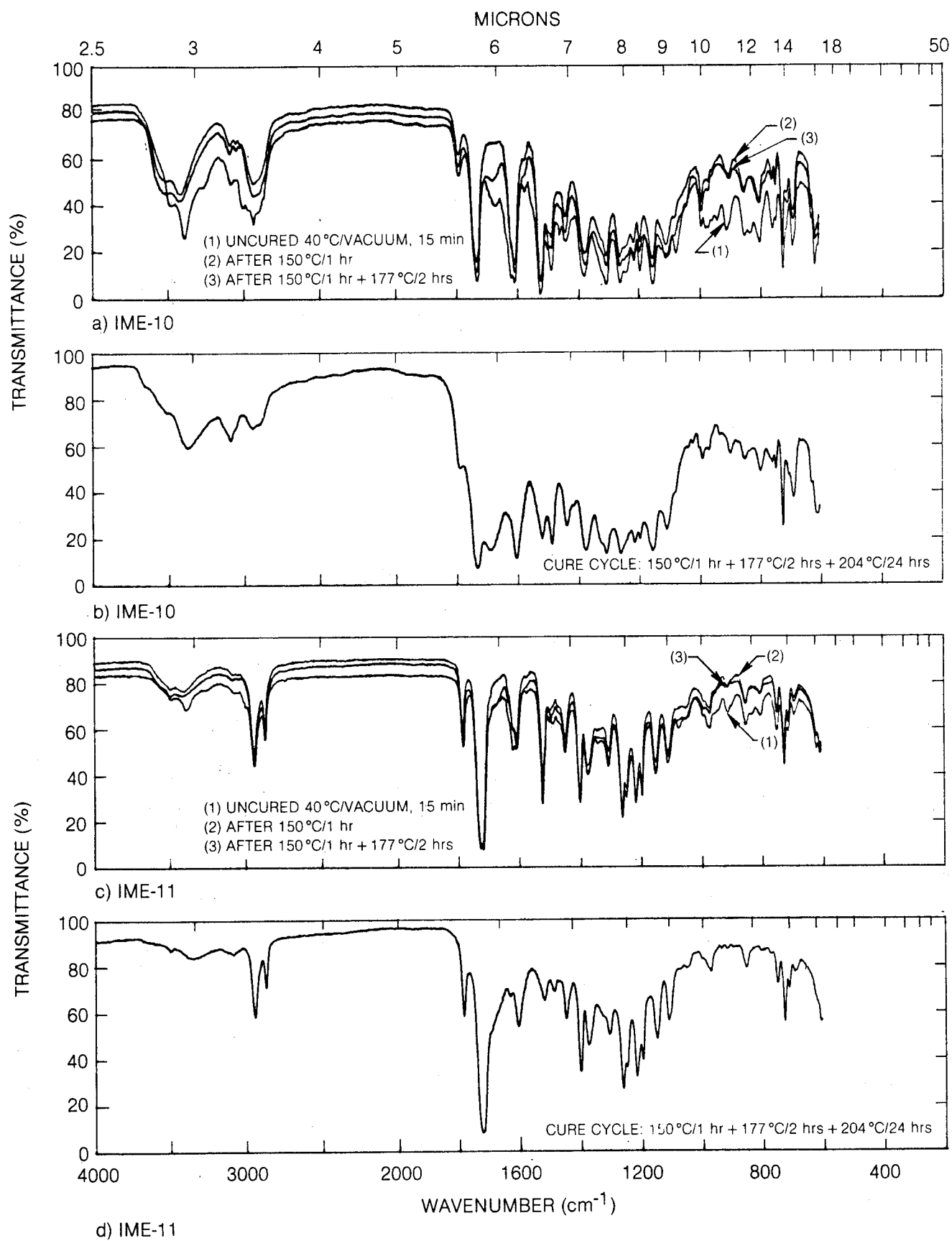


c) BISIMIDE AMINE 6F-3,3'-DDS-1,12-DDA (METHOD E, N189)

## INFRARED SPECTRA OF IME EPOXY RESINS

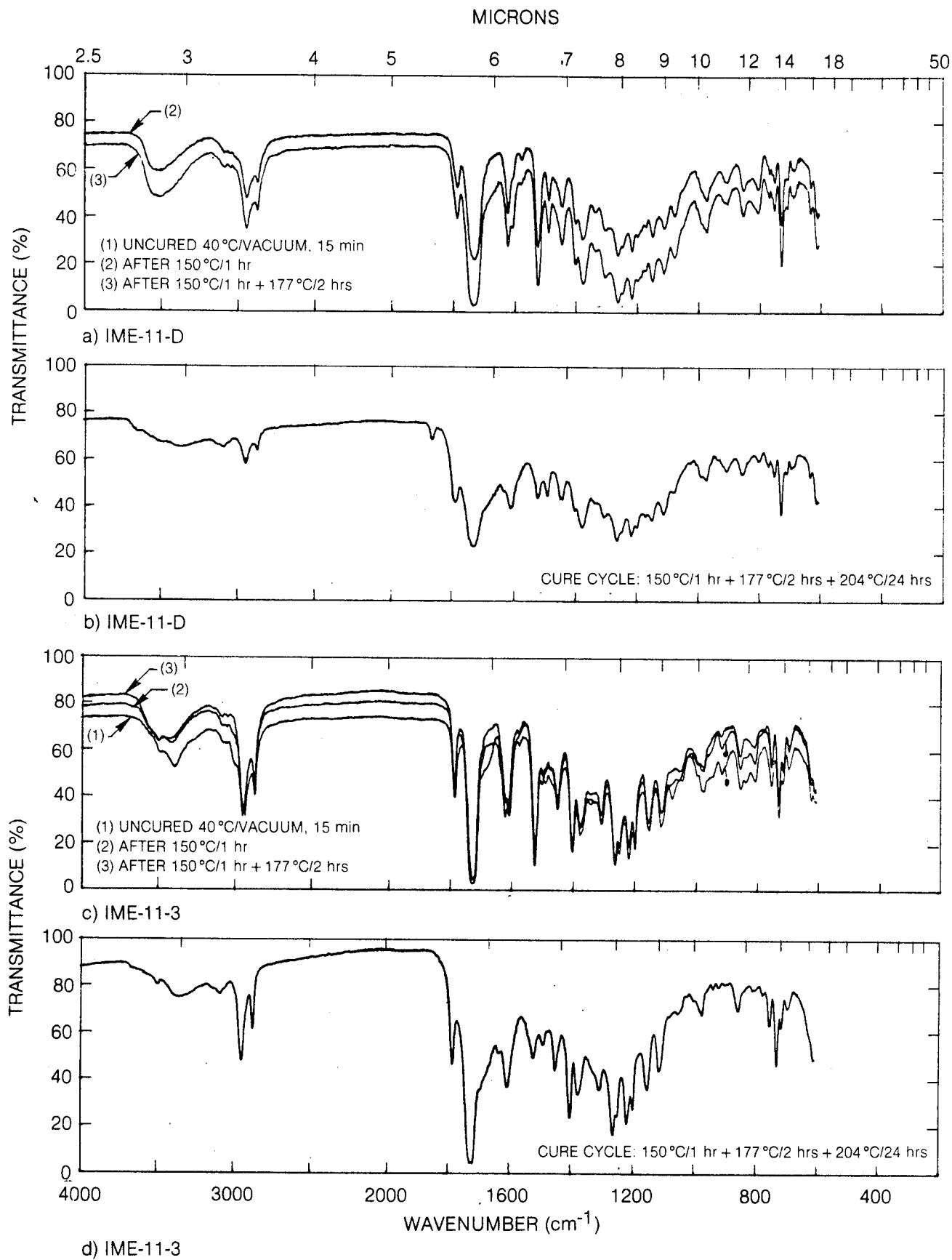


## INFRARED SPECTRA OF IME EPOXY RESINS

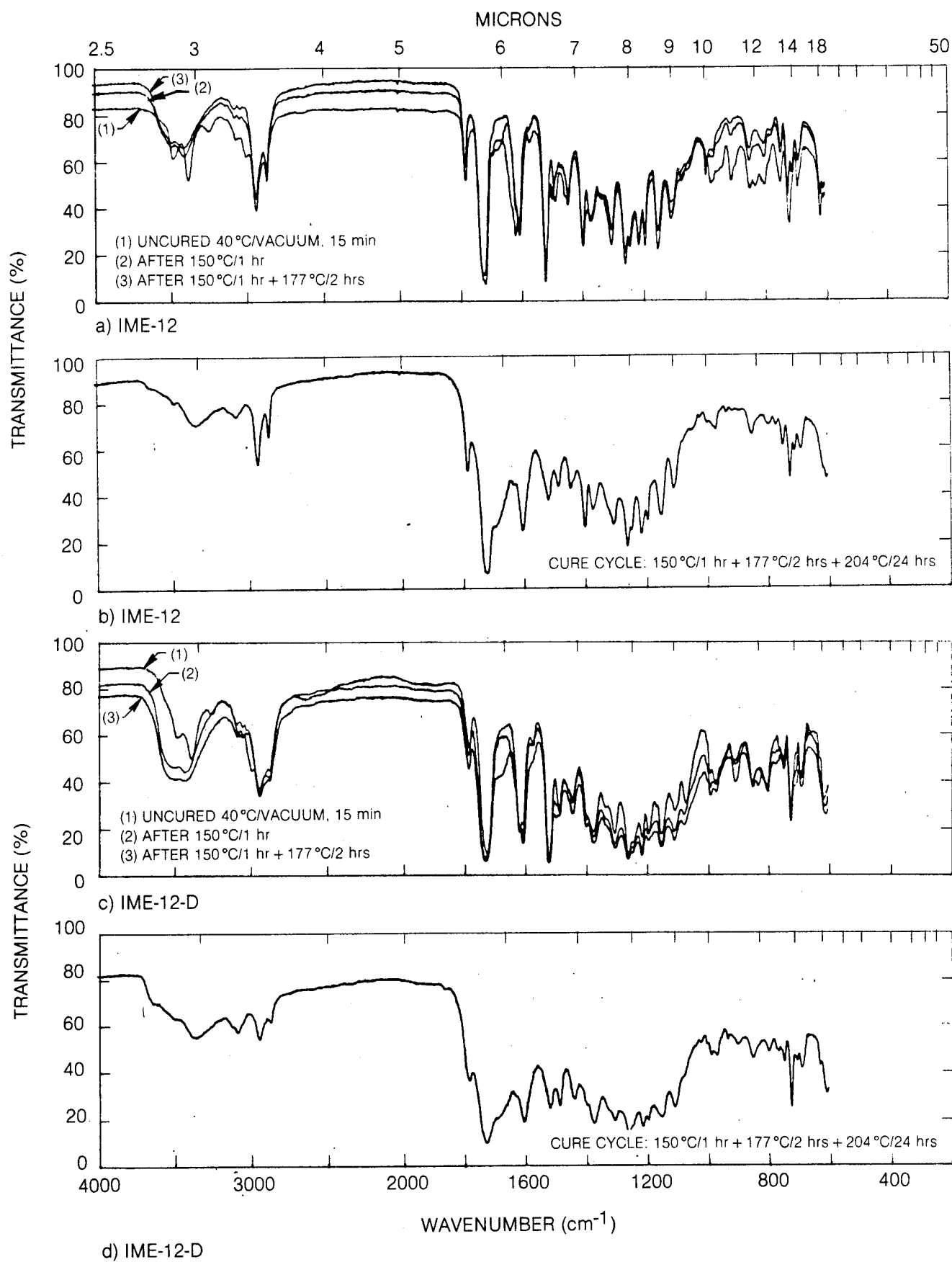




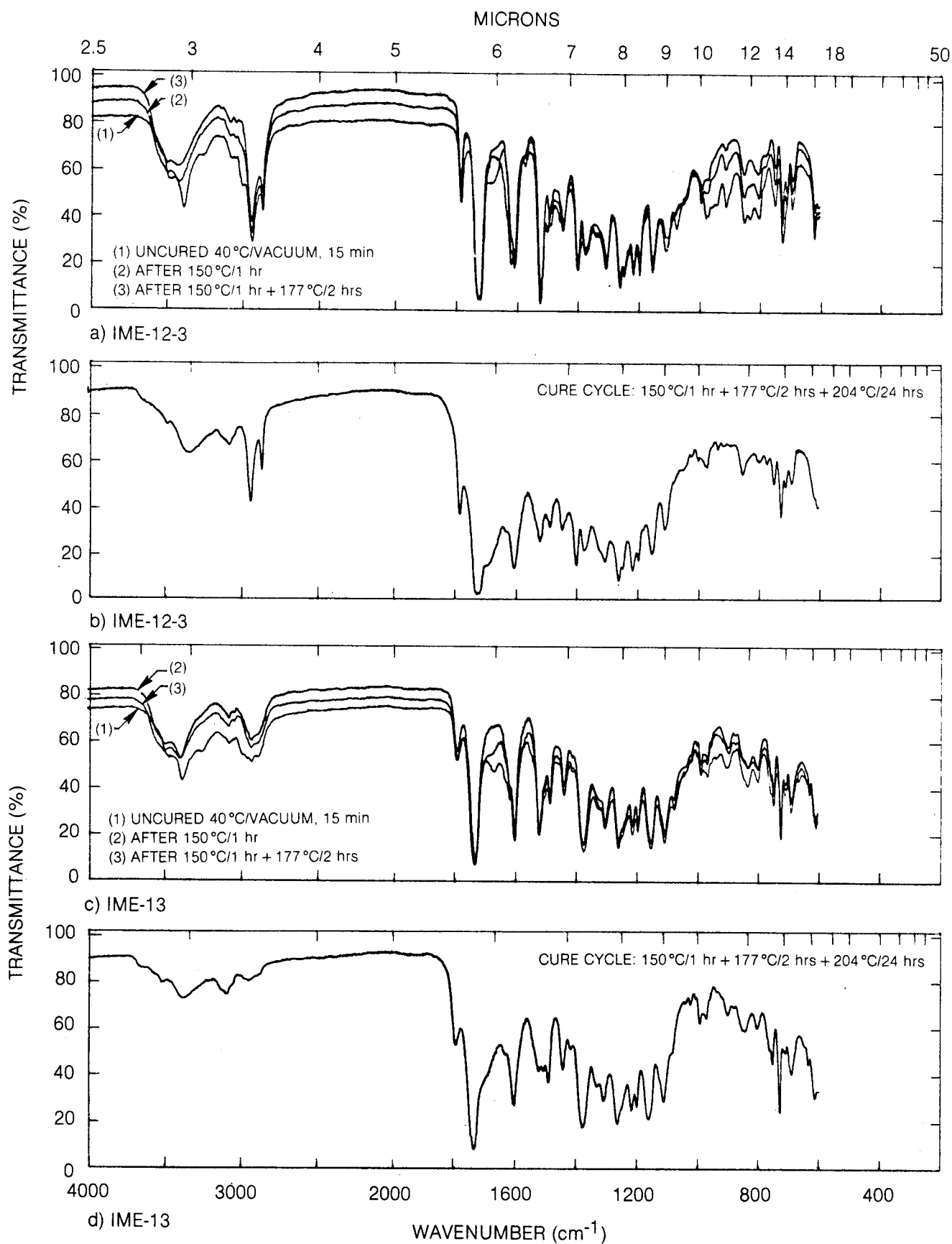
## INFRARED SPECTRA OF IME EPOXY RESINS



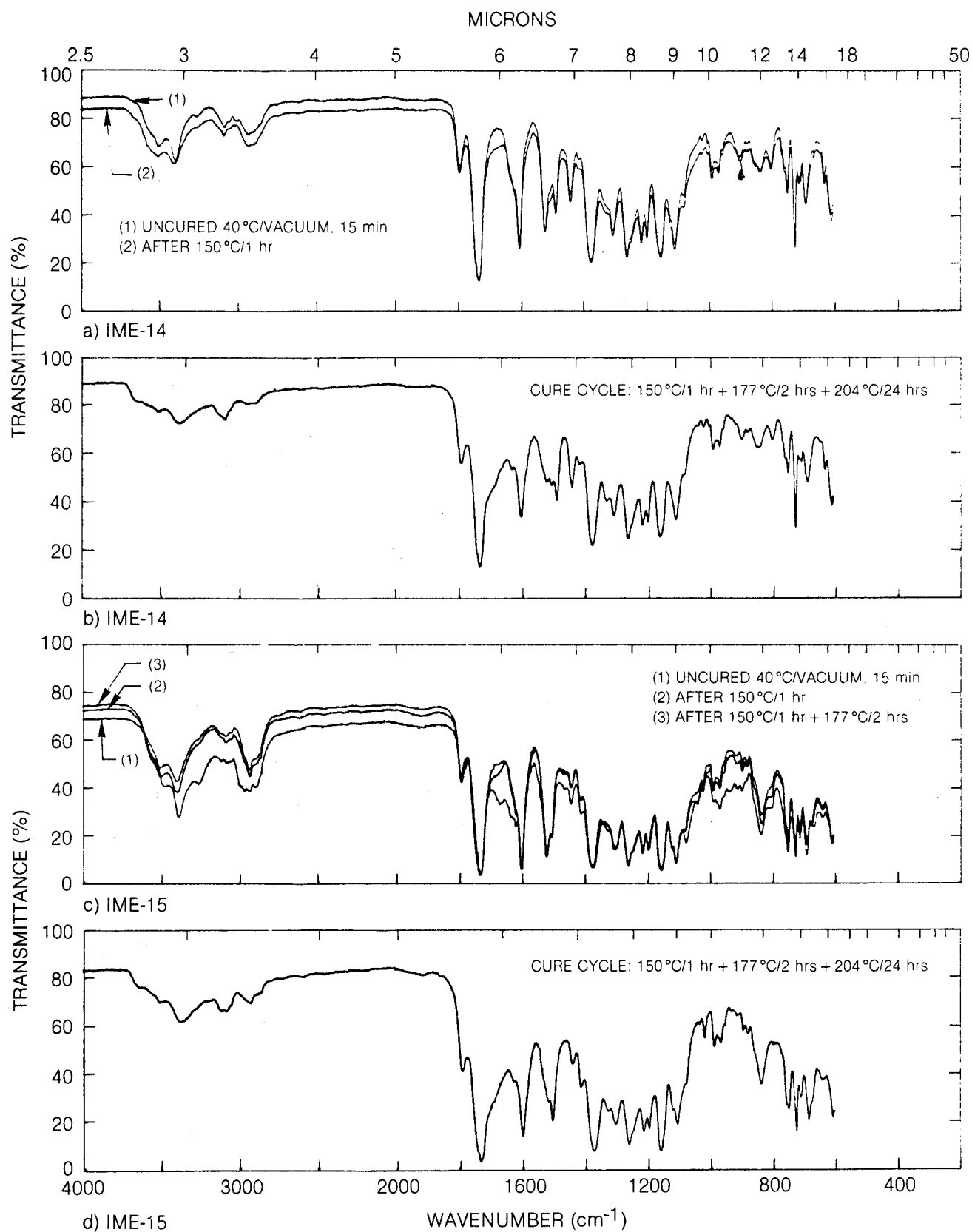
## INFRARED SPECTRA OF IME EPOXY RESINS



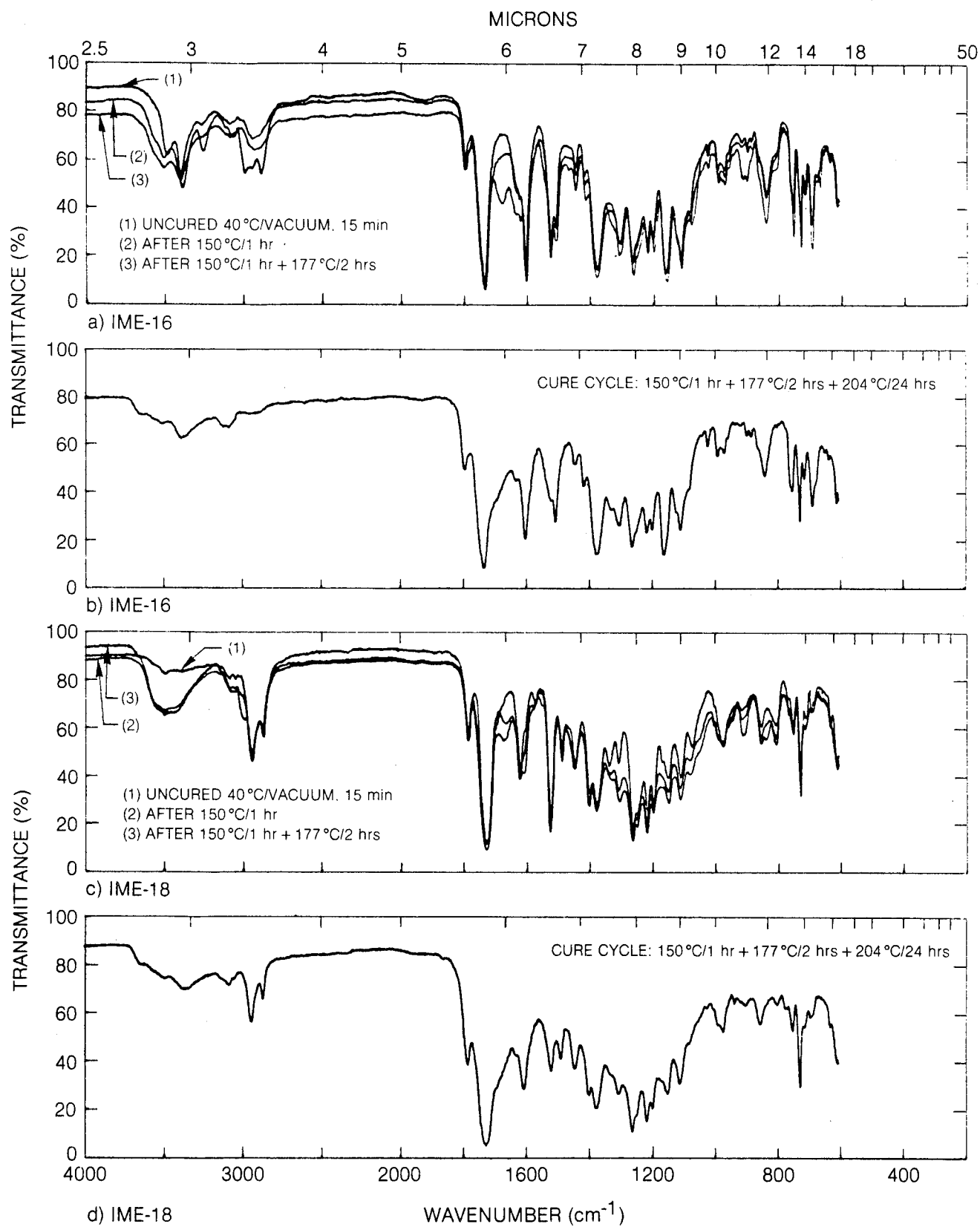
## INFRARED SPECTRA OF IME EPOXY RESINS



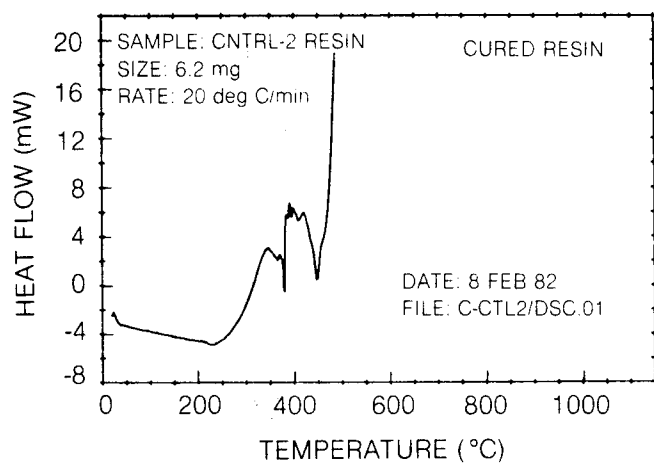
## INFRARED SPECTRA OF IME EPOXY RESINS



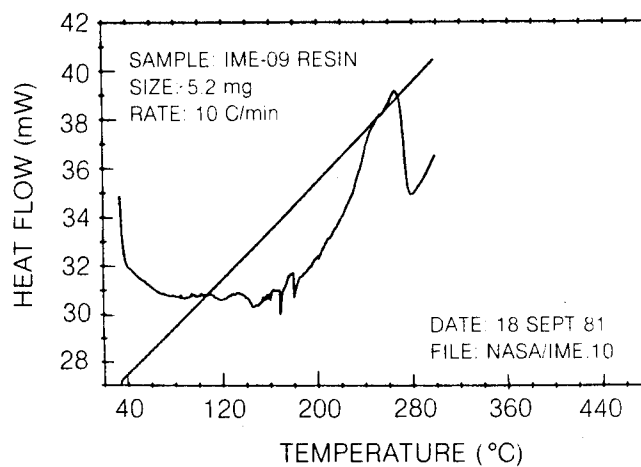
## INFRARED SPECTRA OF IME EPOXY RESINS



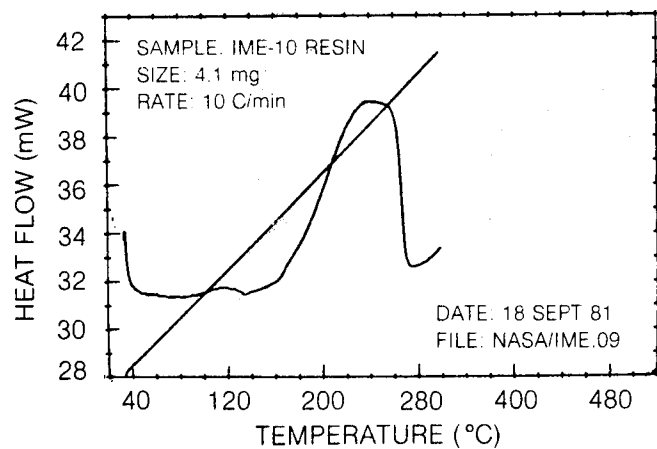
## DSC SCANS OF UNCURED IME RESINS



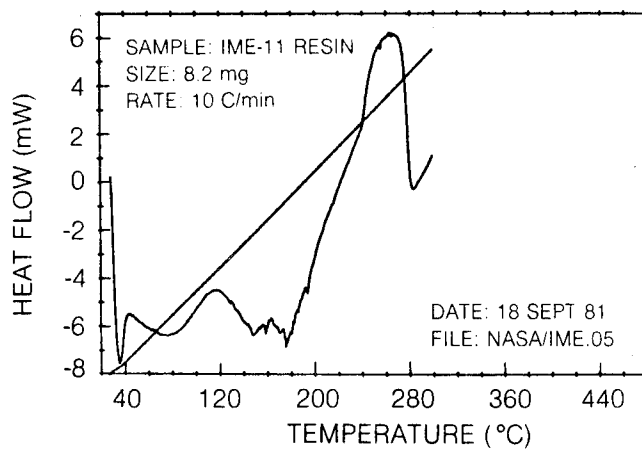
a) CONTROL RESIN C-2



b) IME-9

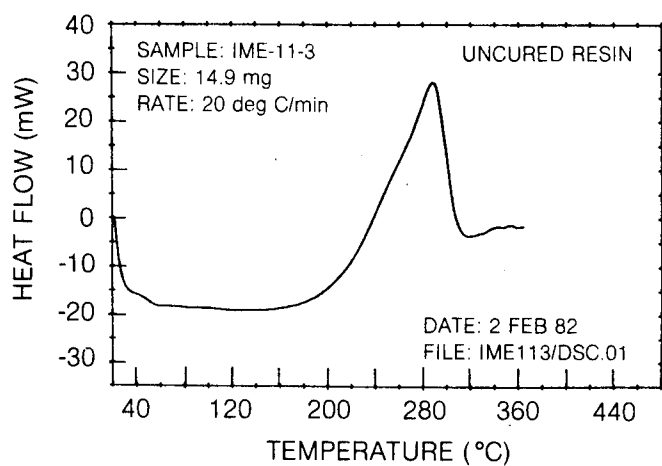


c) IME-10

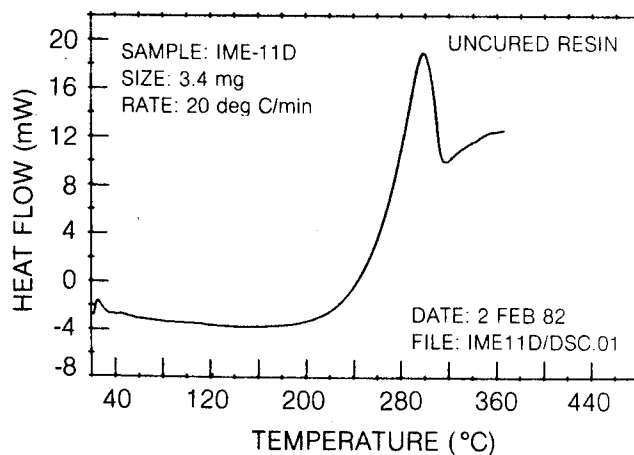


d) IME-11

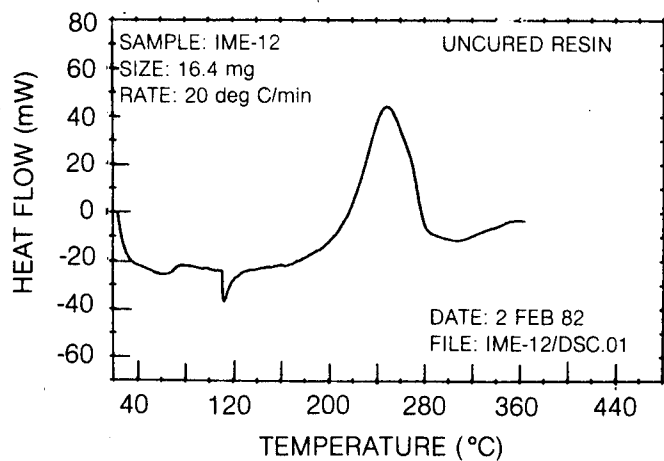
## DSC SCANS OF UNCURED IME RESINS



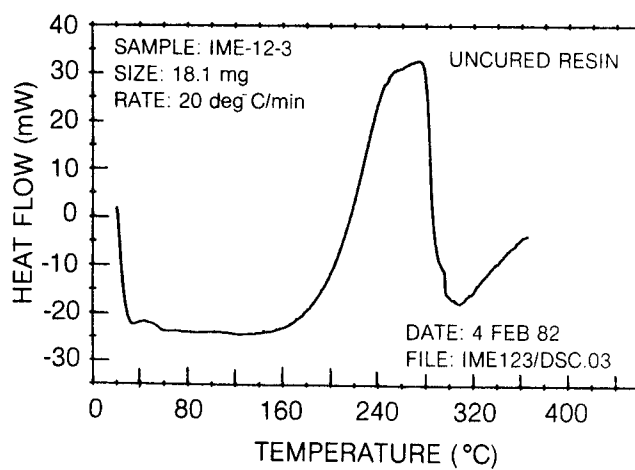
a) IME-11-3



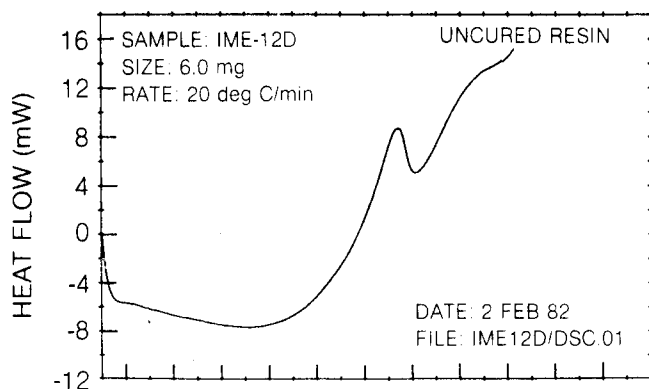
b) IME-11D



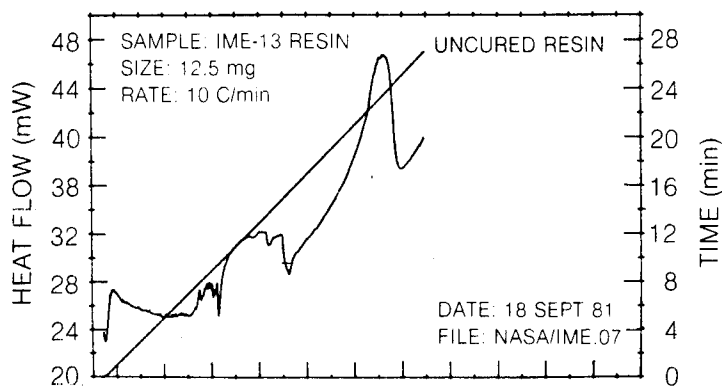
c) IME-12



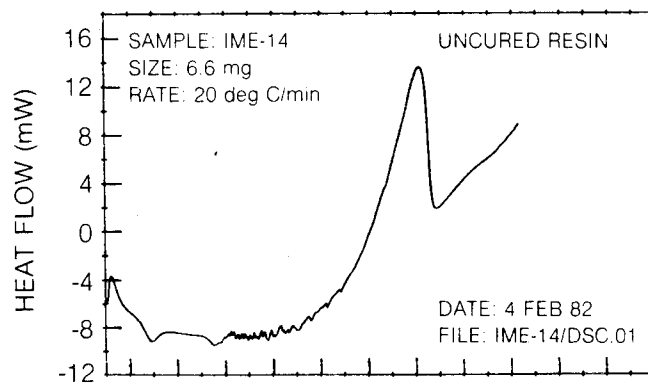
d) IME-12-3

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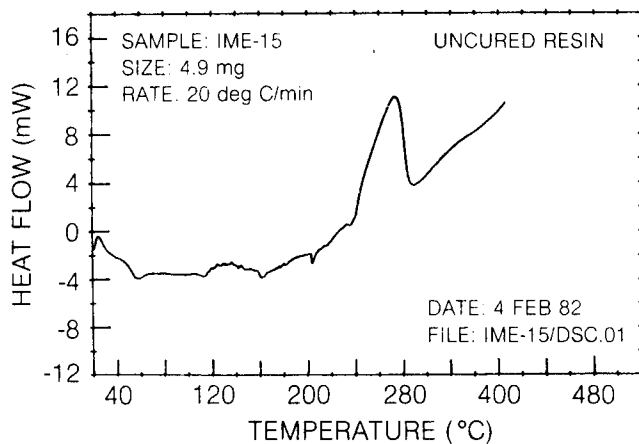
a) IME-12D



b) IME-13

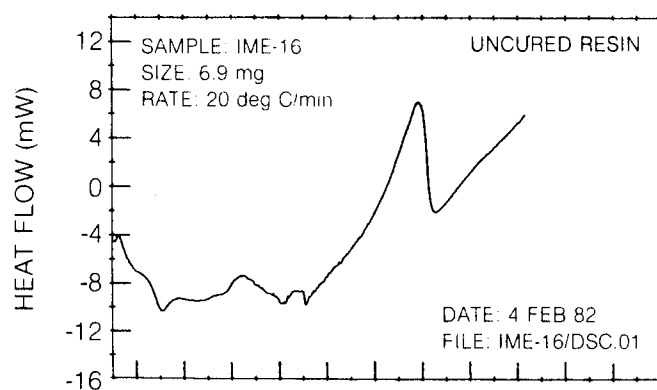


c) IME-14

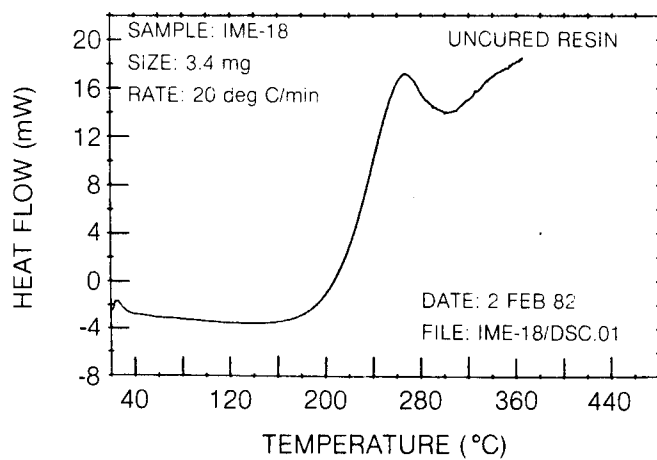


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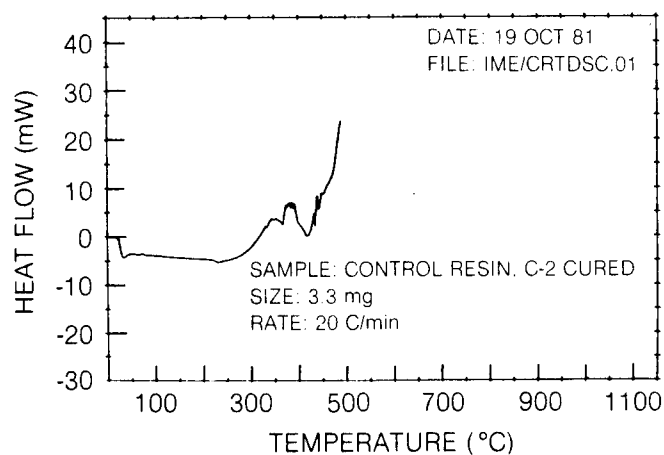
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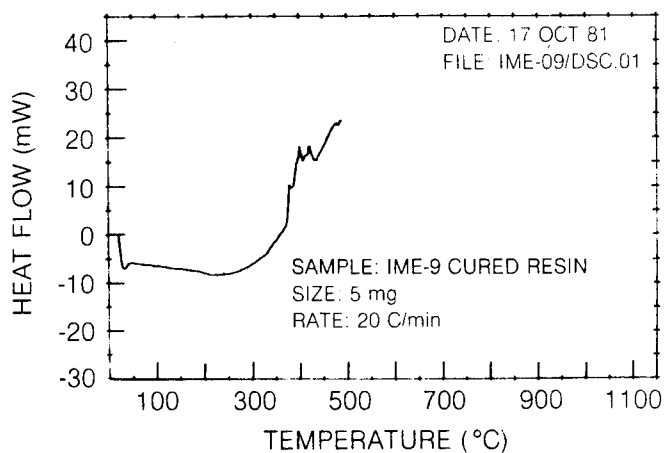


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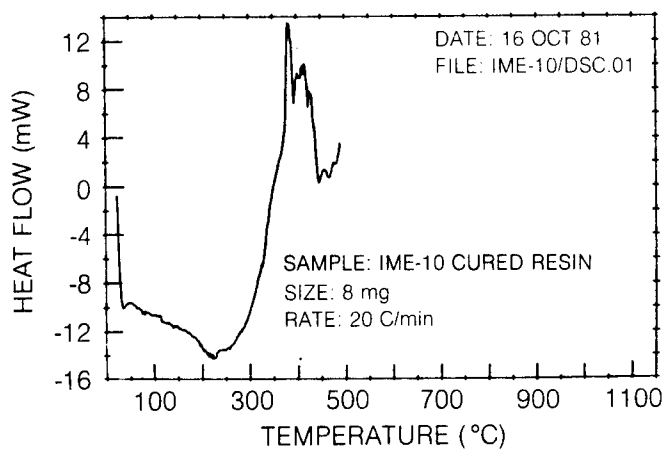
## DSC SCANS OF CURED IME RESINS



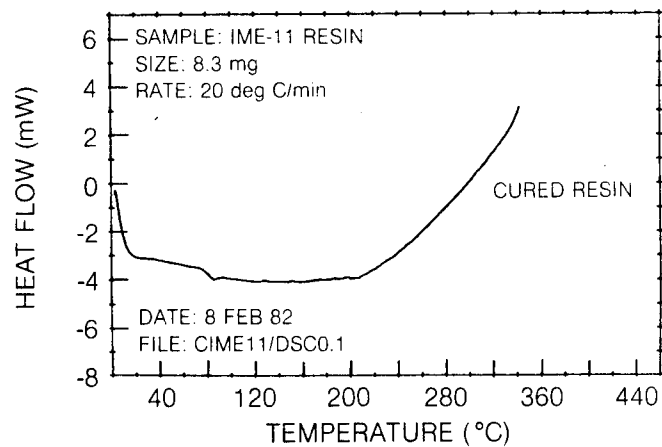
a) CONTROL RESIN C-2



b) IME-9

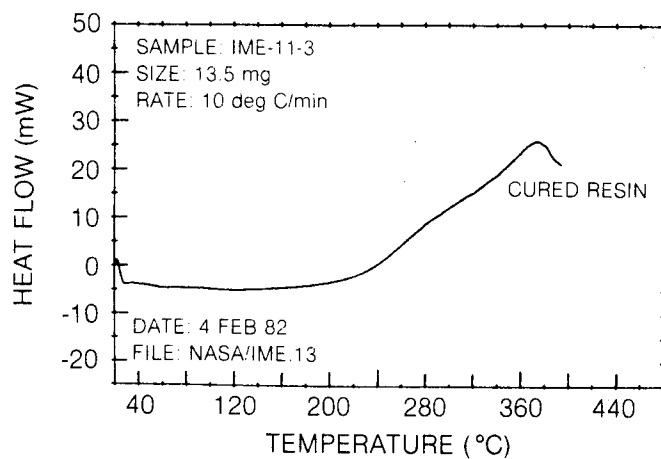


c) IME-10

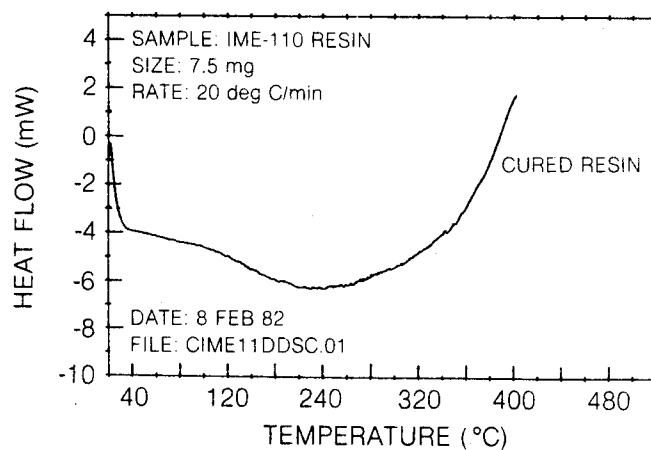


d) IME-11

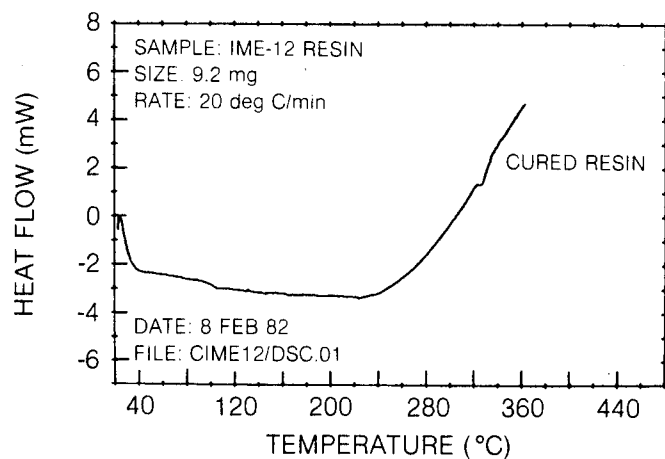
## DSC SCANS OF CURED IME RESINS



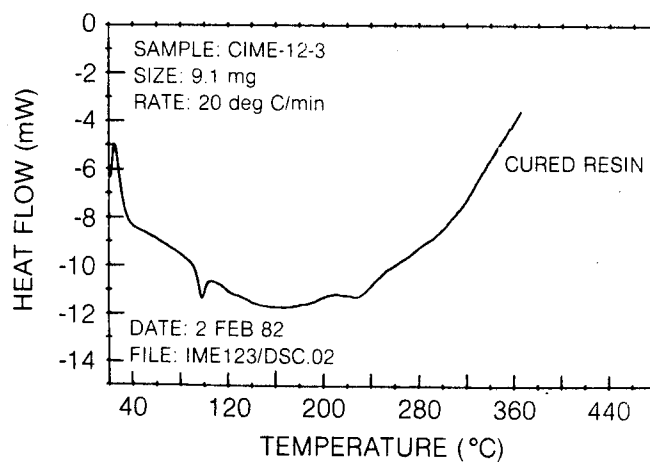
a) IME-11-3



b) IME-11D

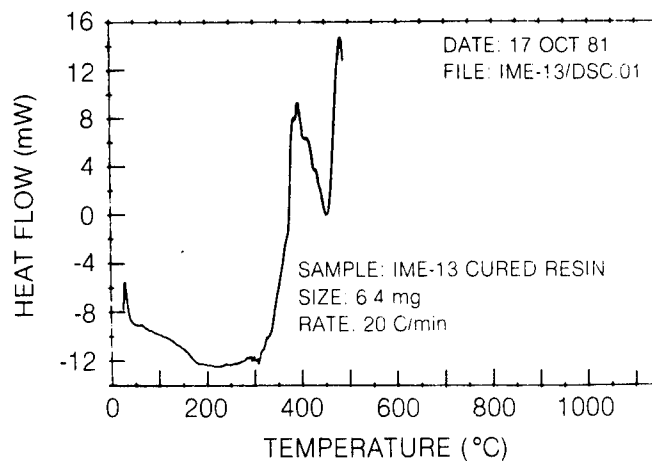
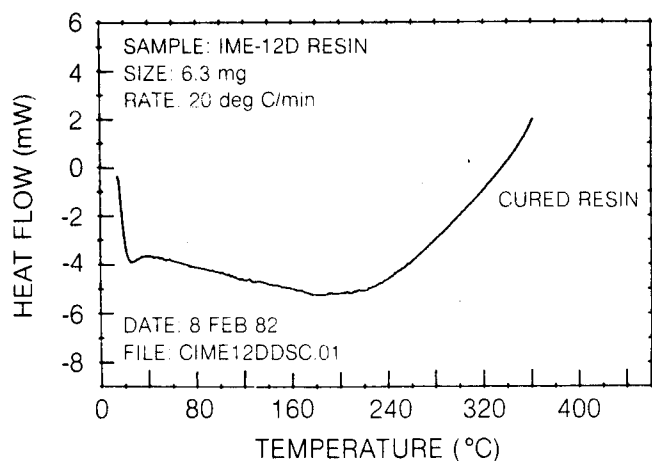


c) IME-12



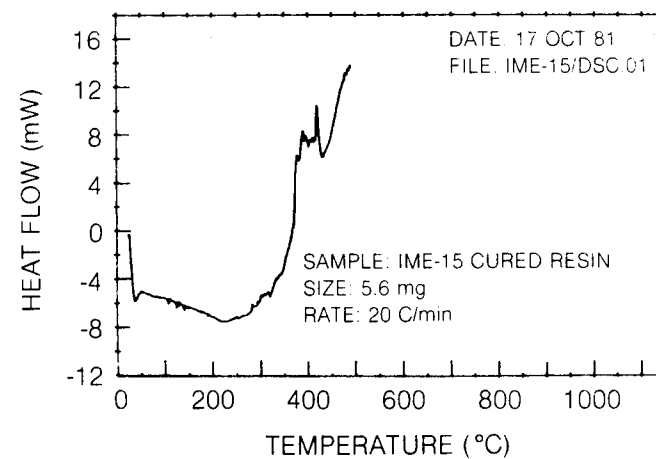
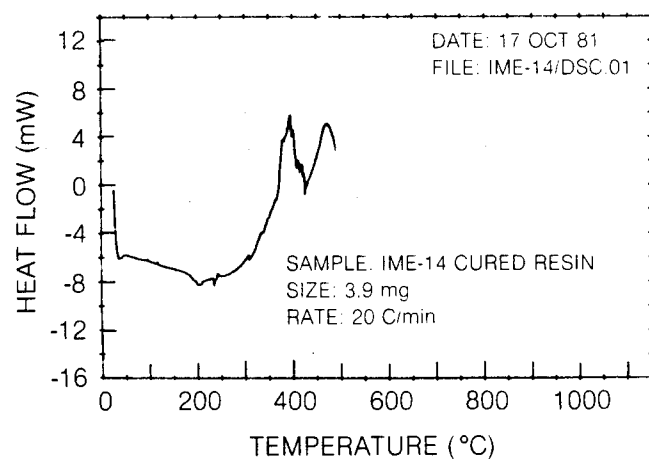
d) IME-12-3

## DSC SCANS OF CURED IME RESINS



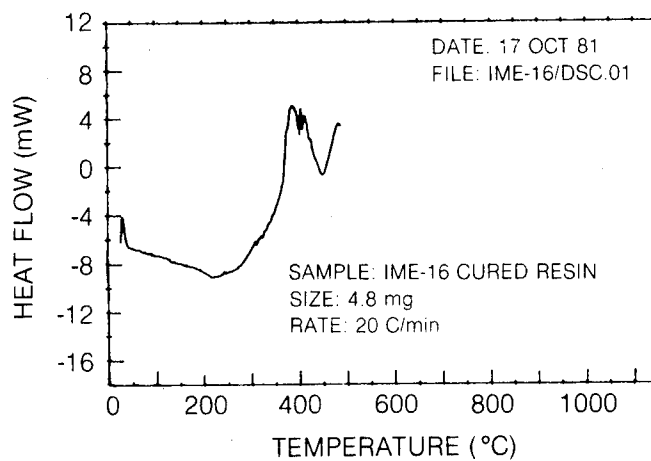
a) IME-12D

b) IME-13



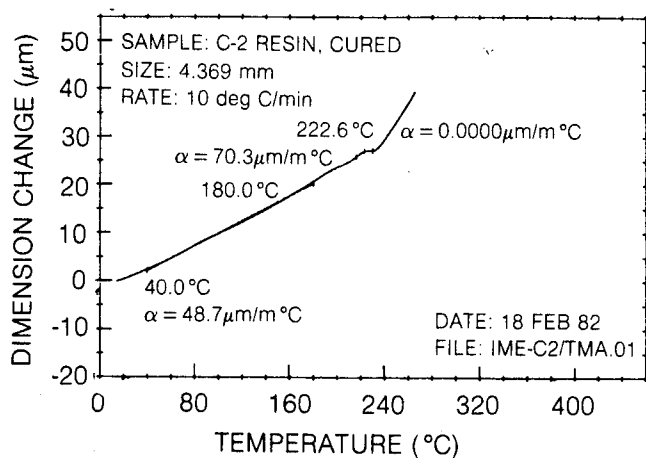
c) IME-14

d) IME-15

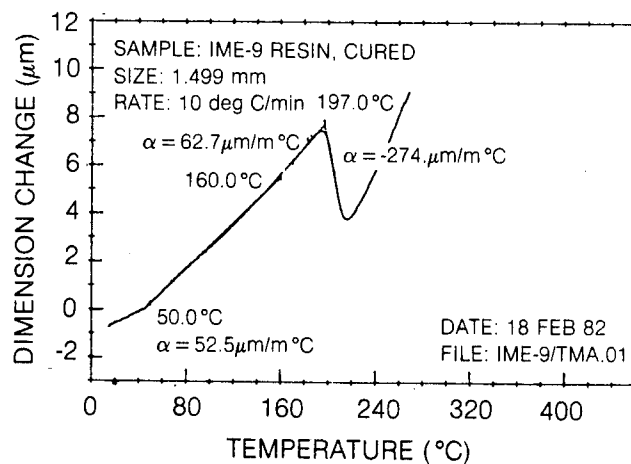


e) IME-16

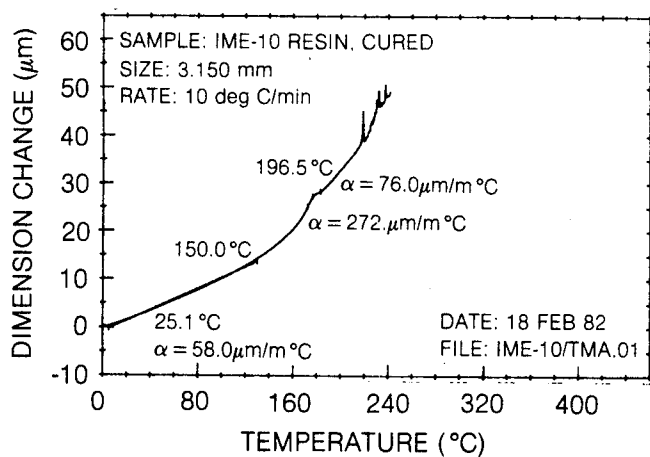
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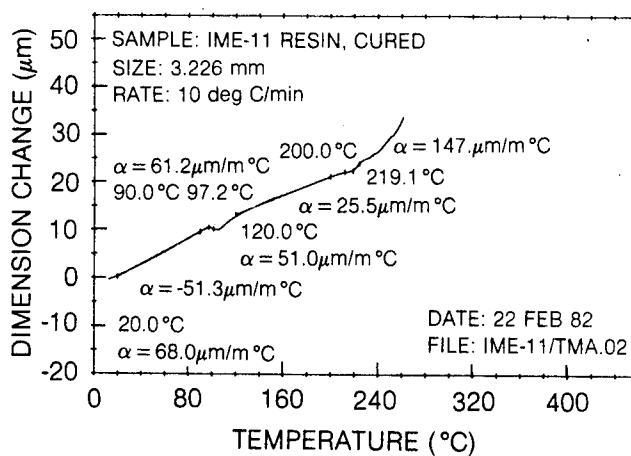
a) CONTROL RESIN C-2 (MY720/3,3'-DDS)



b) IME-9

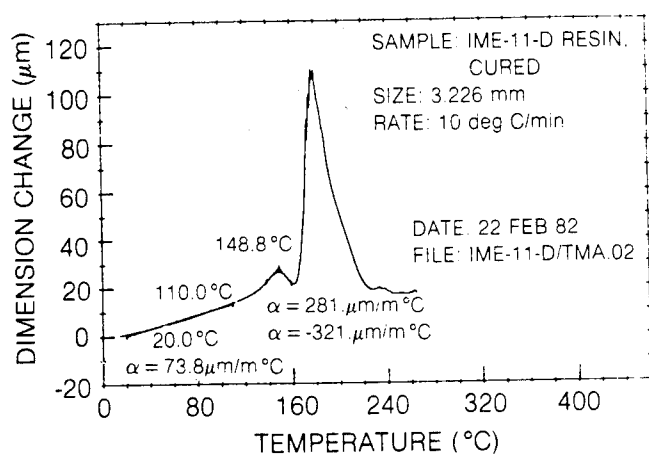


c) IME-10

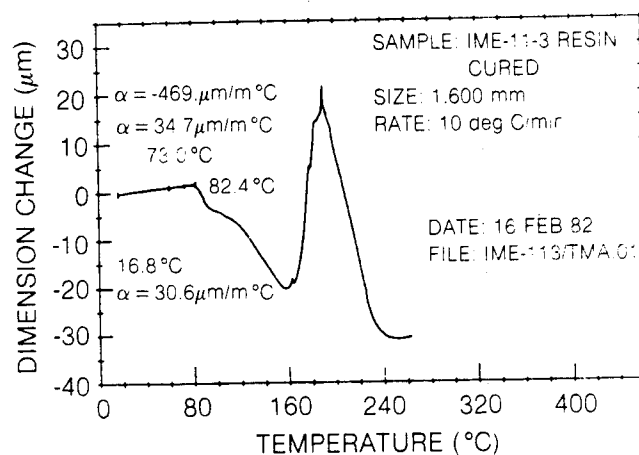


d) IME-11

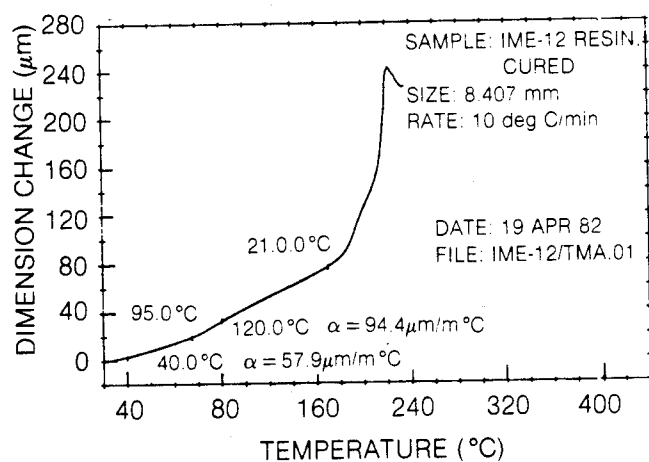
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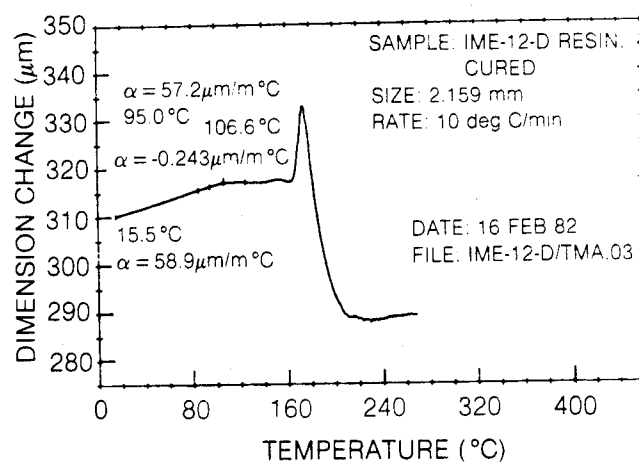
a) IME-11-D



b) IME-11-3

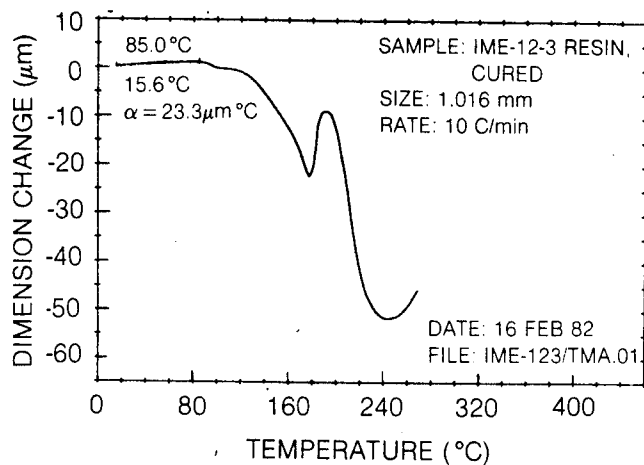


c) IME-12

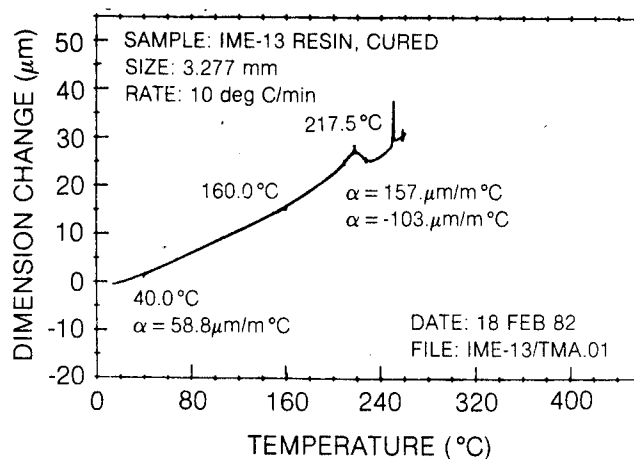


d) IME-12-D

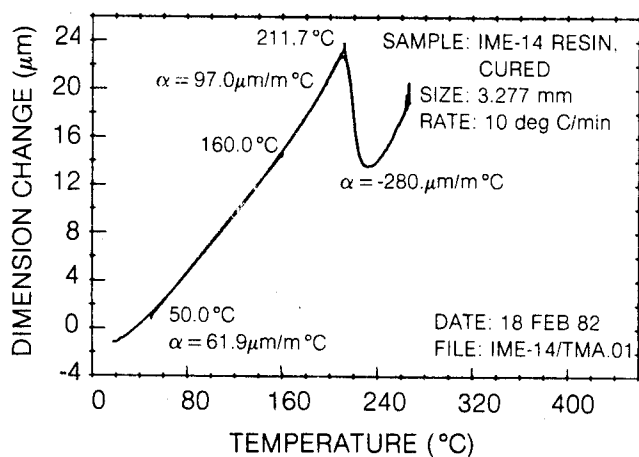
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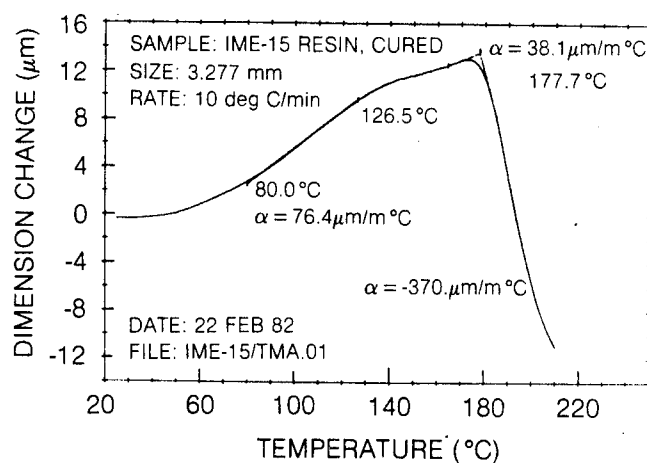
a) IME-12-3



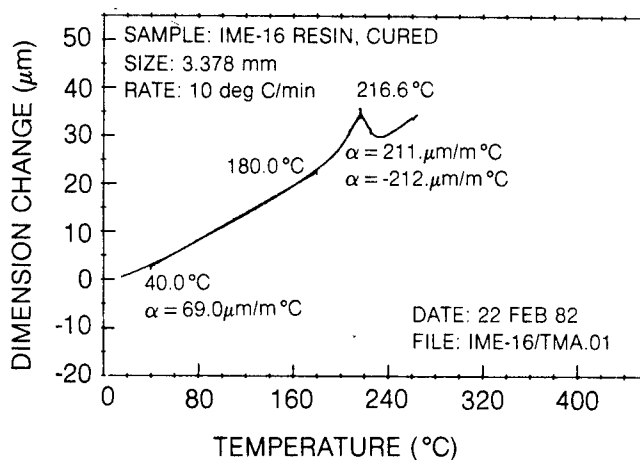
b) IME-13



c) IME-14



d) IME-15

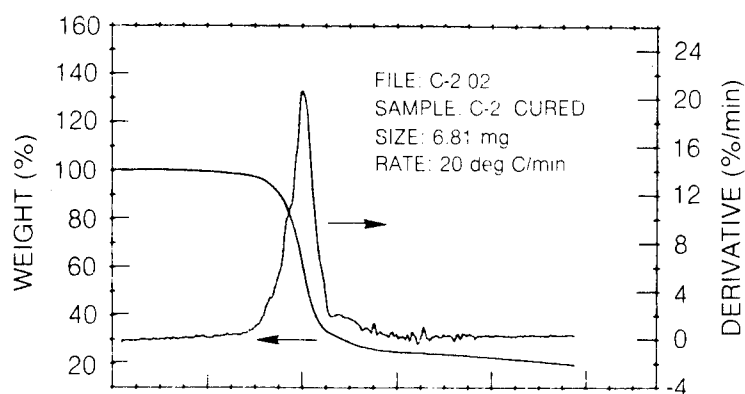


e) IME-16

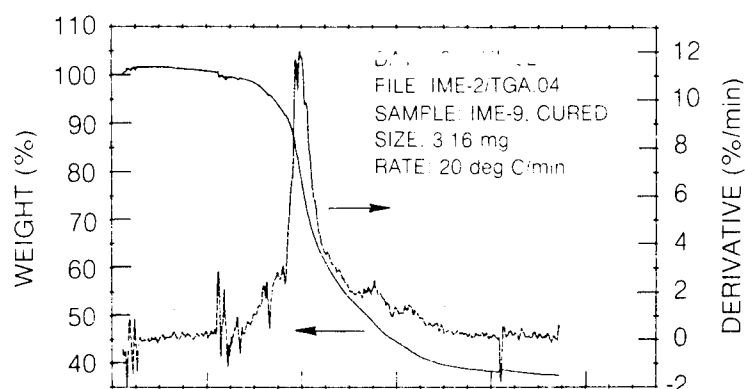
# THERMOGRAVIMETRIC ANALYSIS (TGA) OF CURED IME RESINS

FIG. 36

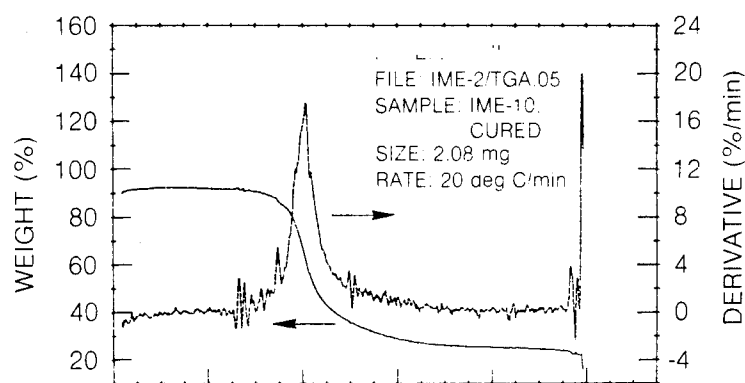
NITROGEN ATMOSPHERE



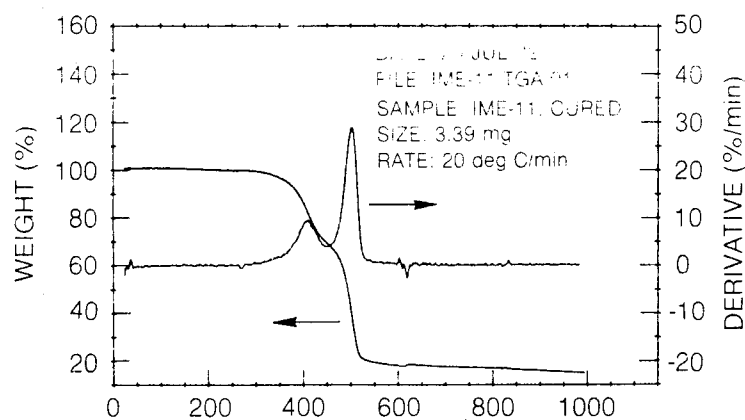
a) CONTROL RESIN C-2



b) IME-9



c) IME-10



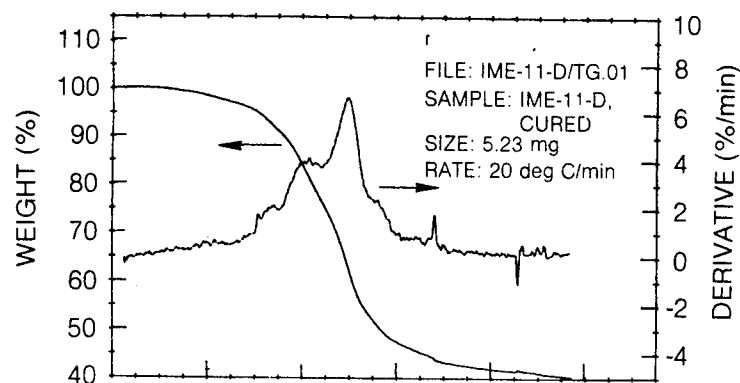
d) IME-11

TEMPERATURE (°C)

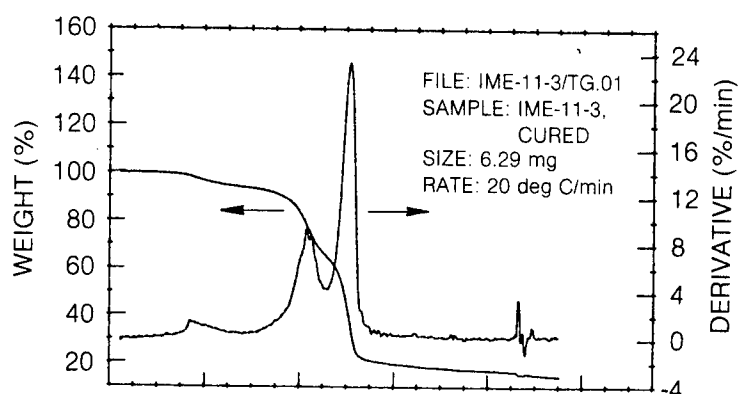


# **THERMOGRAVIMETRIC ANALYSIS (TGA) OF CURED IME RESINS** **NITROGEN ATMOSPHERE**

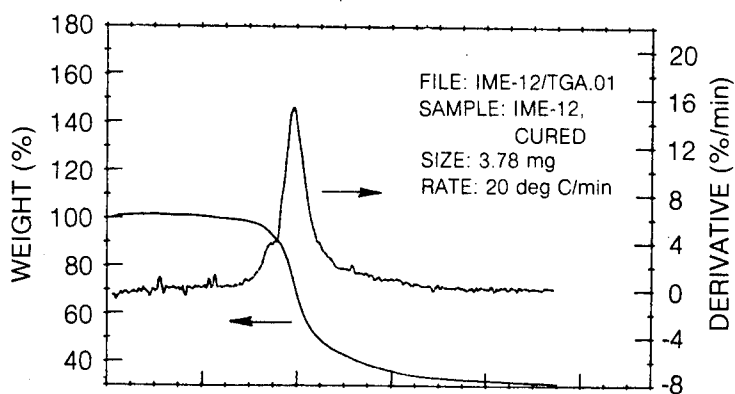
FIG. 37



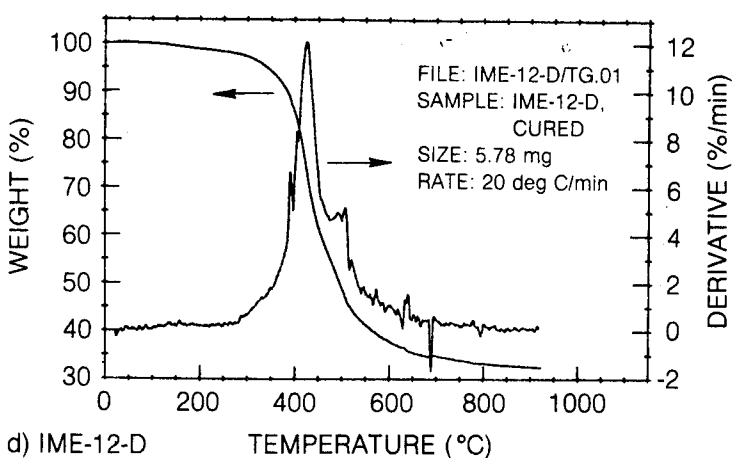
a) IME-11-D



b) IME-11-3



c) IME-12

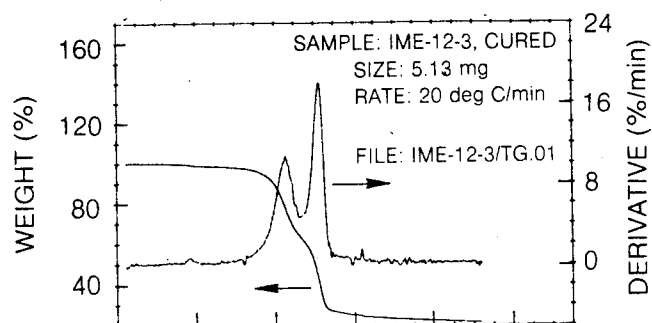


d) IME-12-D

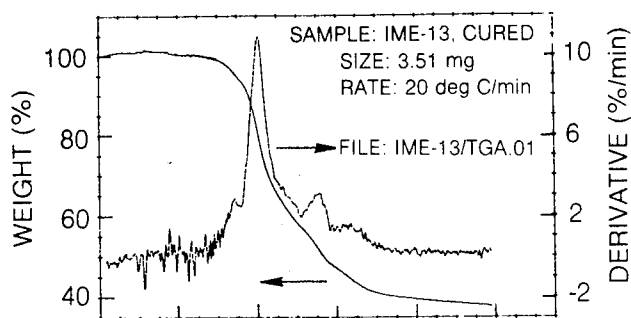
TEMPERATURE (°C)

## THERMOGRAVIMETRIC ANALYSIS (TGA) OF CURED IME RESINS

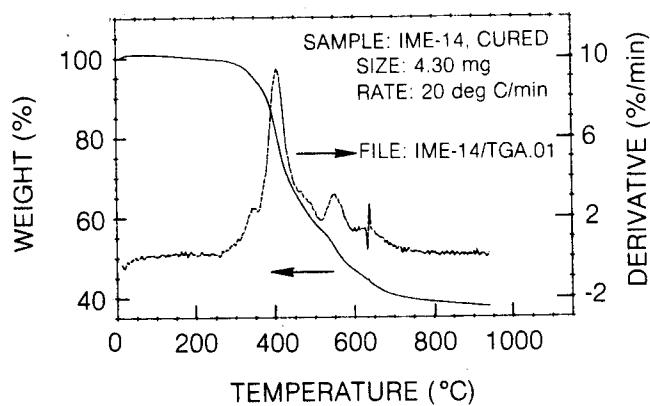
NITROGEN ATMOSPHERE



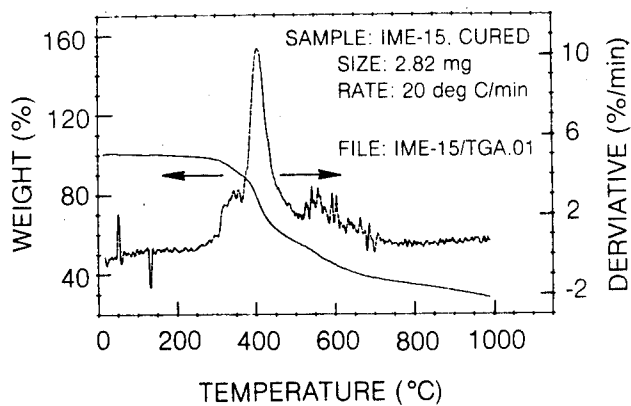
a) IME-12-3



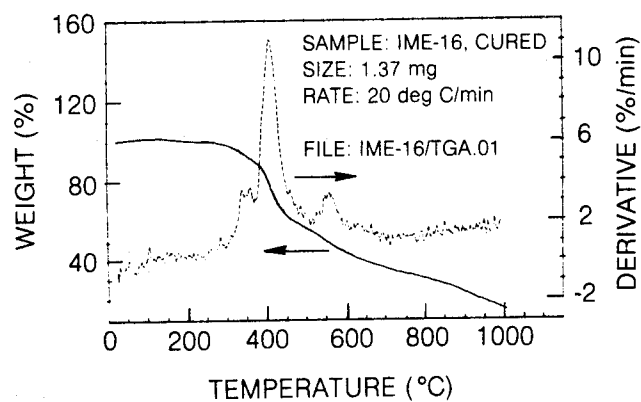
b) IME-13



c) IME-14



d) IME-15



e) IME-16

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